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NEW SYNTHETIC METHODS FOR SILICON-NITROGEN POLYMERS

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Midwest Research Institute

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NEW SYNTHETIC METHODS FOR SILICON-NITROGEN POLYMERS

L. W. Breed, J. C. Wiley, Jr., and R. L. Elliott

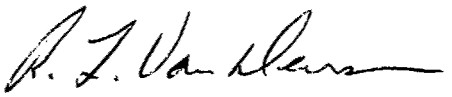
FOREWORD

This report was prepared by Midwest Research Institute, 425 Volker Boulevard, Kansas City, Missouri 64110, under USAF Contract No. F33615-71-C-1235, "Research on New Synthetic Methods for Silicon-Nitrogen Polymers." The contract was initiated under Project No. 7342, "Fundamental Research on Macromolecular Materials and Lubrication Phenomena," Task No. 734201, "Basic Factors in the Synthesis of Macromolecular Materials." The work was administered under the direction of the Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, with Dr. Harold Rosenberg, AFML/MBP, as Project Scientist.

This technical report covers the work conducted from 31 January 1971 to 31 January 1972. The report was submitted by the authors in February 1972.

The work was carried out by Messrs. Richard L. Elliott, J. C. Wiley, Jr., and L. W. Breed, who acted as principal investigator.

This technical report has been reviewed and is approved.



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ABSTRACT

If phenothiazine is present in the monomer mixture, arylenedisilanols and cyclosiloxazanes, with p-phenylenebis(methylvinylsilanol) present to insure crosslinking sites, provide polymers with inherent viscosities up to 3.5 dl/g. The polymers can be compounded and cured by conventional procedures. Condensation products of oxydi-p-phenylenebis(dimethylsilanol) and cyclosiloxazanes were studied in detail and elastomers with ultimate tensile strengths of 600-800 psi and 50-150% elongation at break were obtained. Some polymers were also prepared from p-phenylenebis(dimethylsilanol). Depending on the particular structure the polymers retained 15-70% of their strength after 24 hr at 250°C in a closed vessel and 60-80% of their strength after 500 hr in a circulating air oven at 260°C. Exposed to water-saturated air at 65-95°C for 500 hr they retained 45-65% of their strength. Brittle points as low as -100°C were obtained. The first event in the thermal decomposition of these polymers in air is methyl group oxidation. The polymer with the widest range of useful properties was prepared from p-phenylenebis(dimethylsilanol) and decamethyl-1,5-dioxa-3,7-diaza-2,4,6,8-tetrasilacyclooctane. Polymers from arylenedisilanols and cyclodisilazane monomers either gave very low strength elastomers or could not be cured. Improved methods of synthesis for a number of the monomers are reported.

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I.

INTRODUCTION

The goal of this program has been to develop new synthetic methods for high molecular weight silicon-nitrogen polymers. Approaches were chosen that afforded the greatest probability of obtaining polymers with flexible backbones. In order that the polymers may have a high order of thermal and hydrolytic stability, polymer structures and their precursors have chiefly been selected from the groups that include trisilylamines, N,N'-substituted cyclodisilazanes, and siloxazanes. Such polymers were expected to provide candidate materials for further development into high temperature, high performance elastomers or coatings for use in extreme environments for aircraft and missile applications.

In previous work, a number of monomeric structures have been prepared and procedures for incorporating them into polymers have been examined. It was of particular interest that N,N'-bis[(dialkylamino)dimethylsilyl]tetramethylcyclodisilazane condensed with oxydi-p-phenylenebis(dimethylsilanol) with the formation of storage-stable, toluene-soluble polymers with good heat stability, provided the compositions were suitably end-capped with bis(trimethylsilyl)acetamide. When the dimethylamino derivatives of the cyclodisilazanes were used, polymers with inherent viscosities of 0.3 dl/g were obtained; when the diethylamino derivatives were used, polymers with inherent viscosities as high as 0.9 dl/g were obtained. These polymers had improved, but still apparently inadequate, hydrolytic stability.

New vinyl-substituted arylenedisilanols were prepared. When these monomers were incorporated in either arylenedisilanol-cyclosiloxazane or arylenedisilanol-aminosilylcyclodisilazane polycondensation mixtures, the resulting gums could be cured with peroxides by conventional techniques.

In recent work, a method was developed for preparing phenyl, vinyl, ethyl, and 3,3,3-trifluoropropyl-substituted cyclodisilazane derivatives suitable for use in polymerizations. The 3,3,3-trifluoropropyl derivative was of particular interest because its polymer would be expected to show improved solvent resistance and hydrolytic stability.

Although a minor amount of work continued during this report period on new monomers, the work described in this report is chiefly concerned with the correlation of the properties of these new polymer systems with their structures. Because of the more ready accessibility of monomers, most of the effort was on arylenedisilanol-cyclosiloxazane condensates. Also work was necessary on the improvement in the synthetic procedures for the preparation of required monomers.

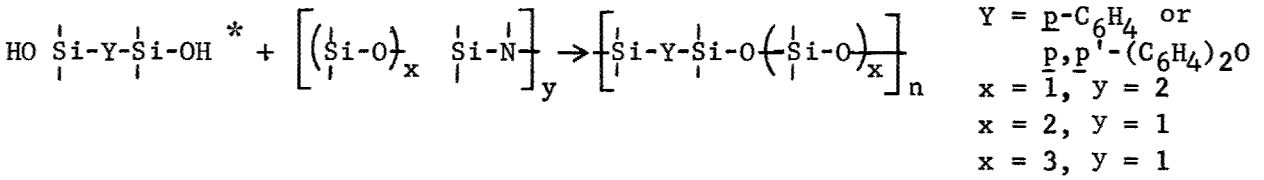
II.

DISCUSSION OF EXPERIMENTAL RESULTS

The work covered in this report is largely concerned with the development of compounded and cured elastomeric compositions based on experimental polymer systems prepared in earlier work under Air Force contract. A small laboratory mill was acquired for this purpose, and a number of the necessary monomers were prepared.

Two polymer systems were of particular interest: (a) condensates of arylenedisilanols and cyclosiloxazanes modified with vinyl-containing monomers to provide crosslinking sites, and (b) condensates of arylenedisilanols and dialkylamino-functional cyclodisilazane derivatives, particularly those with 3,3,3-trifluoropropyl substitution, also modified with vinyl-containing monomers to provide crosslinking sites. The first class was selected for primary examination because of the better availability of monomers, the greater certainty of hydrolytic stability of the polymers; and the greater probability of obtaining high molecular weight gums.

A. Arylenedisilanol-cyclosiloxazane Condensates



In the arylenedisilanol-cyclosiloxazane series, six polymers modified with a vinyl-substituted arylenedisilanol co-monomer had been prepared earlier and no particular difficulties had been encountered. One of these polymers had been forwarded to the Materials Laboratory, and it was satisfactorily compounded and cured. The molecular weights on these polymers were not particularly high, but equimolar quantities of the monomers had been used in the polymerizations. Since some of the cyclosiloxazane may be lost during the polymerization by volatilization, higher molecular weights can usually be obtained in this system through the use of an excess of siloxazane.

When the present work was initiated to prepare polymer samples for curing studies, a number of problems were encountered that had not been anticipated. These problems related chiefly to the crosslinking, or loss of solubility of the polymers in toluene, during polymerization. A

* In structural formulas all unfilled valences indicate methyl groups.

considerable effort was devoted to the consideration of the various factors that could lead to this loss of solubility.

1. Arylenedisilanol purity: When new polymeric compositions similar to ones that had been prepared earlier proved to be toluene-insoluble, the arylenedisilanol purity was checked in polymerizations compositions not containing vinyl groups. Some of these compositions also gave toluene-insoluble polymers. On reexamination of previous experimental reports (Ref. 1a), it was found that half the required monobasic phosphate had been used in the hydrolysis of the sodium salt in the preparation of the oxydi-p-phenylenebis(dimethylsilanol). Of the two monomer samples prepared by this method, one gave a soluble polymer, the other did not, although both compounds had the same melting points and infrared spectra. In two subsequent preparations of the monomer, the error had been repeated, and both of these monomers gave toluene-insoluble polymers.

Upon rehydrolysis of these samples with the proper amount of monobasic potassium phosphate, soluble polymers were obtained consistently. No analytical method has been found that will differentiate arylenedisilanols which do not produce completely soluble polymers, but it can be inferred from these data that the effect is probably one of absorption of a basic species on the arylenedisilanol during its precipitation and the incomplete removal of this trace impurity during the purification procedures.

Since soluble polymers could also be obtained with the same cyclosiloxazane and p-phenylenebis(dimethylsilanol), it was assumed at this point that the problem of solubility loss was not related to the cyclosiloxazane monomers. However, even with the improved oxydi-p-phenylenebis(dimethylsilanol), partly insoluble polymeric condensates continued to be obtained in condensation polymerizations when p-phenylenebis(methylvinylsilanol) or oxydi-p-phenylenebis(methylvinylsilanol) were present. Loss of solubility occurred both at the 2 and 5% levels of vinyl monomer content with and without an excess of the cyclosiloxazane.

2. Procedural variations: In subsequent work, it was observed that if the monomers were very carefully mixed during the early stages of the polymerizations when the mixtures were relatively mobile, the extent of insolubility reached as high as 85%. This result suggested that the monomers were possibly inadequately mixed in the early experiments and that the effective vinyl concentration may have been much less than the proportion of monomer used in its preparation. When the vinyl concentrations were lowered, soluble polymers were reproducibly prepared with vinyl concentrations up to 1% at 140°C and 0.4% at 160°C. However, all attempts to cure these polymers under conditions that were effective with the original polymers were unsuccessful.

An alternate approach for incorporating the vinyl monomer into the polymer consisted of first condensing the arylenedisilanol and an excess of the cyclosiloxazane then subsequently adding the vinyl monomer to a toluene solution of the condensate and boiling the mixture. Compositions prepared in this manner also did not cure properly.

Along with curing studies on the various vinyl-containing compositions, a series of polymers containing no vinyl monomers was also prepared and screened. In this series, the effect of water-washing the polymer, heating time, and excess cyclosiloxazane on the polymerization was examined. Although all of these polymers could be milled with filler, none of them cured under the usual conditions.

3. Cyclosiloxazane purity: The purity of the cyclosiloxazane monomer had originally not been considered because, in the absence of the vinyl monomer, soluble polymers had been obtained from a variety of batches. No direct comparison with the original polymerizations was possible since the batch of cyclosiloxazane that had been used in the first experiments had been exhausted. The cyclosiloxazane used in these experiments was not 100% chromatographically pure; yet, this lack of purity had not seemed of too great importance since excesses of the monomer were frequently used in the experiments. Also, no impurities could be detected in the n.m.r. spectra of various fractions of the cyclosiloxazane. In view of the other factors that had been eliminated, it appeared that the problem might result from an interaction between the vinyl monomer and an impurity in the cyclosiloxazane.

When a different cyclosiloxazane, heptamethyl-1,3-dioxa-5-aza-2,4,6-trisilacyclohexane, was substituted for the decamethyl-1,5-dioxa-3,7-diaza-2,4,6,8-tetrasilacyclooctane which had been used in most of the polymerizations, soluble polymers were obtained at the 2 and 5% vinyl levels when no excess of cyclosiloxazane was present. In attempts to increase the molecular weights in this system, 5% excess siloxazane was used, but partly insoluble materials were obtained, 13% insoluble at the 2% vinyl level and 56% at the 5% vinyl level. The soluble polymers cured satisfactorily in much the same way as original polymers had. Thus, it was possible to prepare relatively low molecular weight, curable polymers, provided that the purity of the arylenedisilanol was satisfactory and that only certain cyclosiloxazanes were employed and the latter were not used in excess of the stoichiometric amount.

With these restrictions, a series of polymers could be prepared for screening. The series contained the vinyl monomer at the 1, 2, and 5% levels, and in order to increase the molecular weights at least to some extent, excess cyclosiloxazane was employed at the 1 and 2% levels with 1% of the vinyl monomer. The composition containing the 2% excess cyclosiloxazane became partly insoluble during the polymerization, indicating

the inherent restriction upon the polymer composition with the system as it was being employed.

4. Inhibition of vinyl polymerization: The foregoing work demonstrated that the purity of both the arylenedisilanol and the cyclosiloxazane could affect the susceptibility of the polymers to gellation. Although the identity of the cyclosiloxazane could be important, it is most likely that this effect was a result of the ease of purification of the different monomers. Decamethyl-1,5-dioxa-3,7-diaza-2,4,6,8-tetrasilacyclooctane, which was the most difficult to purify of the possible cyclosiloxazanes, had the greatest tendency to cause gellation. As the work progressed it became evident that although the cyclosiloxazane and the arylenedisilanol impurities may have facilitated crosslinking, the gellation occurred as a result of the vinyl-containing monomer.

Shortly after the first series of polymers was prepared, experiments in which a free radical inhibitor was incorporated in the mixture of monomers demonstrated that the difficulty with crosslinking reactions at the 160°C-polymerization temperature could be considerably reduced. Phenothiazine was selected as the inhibitor of choice, and in preliminary experiments 0.1 wt % of phenothiazine prevented gellation of polymer samples when as much as 5 mole % of the vinyl-substituted monomer was present in the mixtures. In later work, some batches containing 0.1% phenothiazine gelled at 160°C when 4.5 mole % of p-phenylenebis(methylvinylsilanol) was present, particularly when the cyclosiloxazane was decamethyl-1,5-dioxa-3,7-diaza-2,4,6,8-tetrasilacyclooctane; however, no instances of gellation were observed at the 2 mole % level regardless of the amount of cyclosiloxazane present or its identity. Polymers with the higher vinyl level could reliably be prepared if the polymerization temperature was lowered to 140°C, but these polymers had somewhat lower molecular weights. By using phenothiazine in the polymerization mixtures, polymers with inherent viscosities of 1.5-3.5 dl/g were prepared, and these high molecular weight polymers had a sufficiently high vinyl content to provide crosslinking sites during the curing step. There was no difficulty in overriding the inhibitor with peroxide during the curing step.

5. Preliminary curing experiments: Early work established that arylenedisilanol-cyclosiloxazane condensates could not be peroxide-cured if the vinyl-containing monomer concentration was below a certain level. The vinyl monomer at the proper level must be incorporated during the polymerization in a random manner along the polymer chain. Encouraging properties were obtained for the low molecular weight polymers prepared and screened prior to the finding that higher molecular weight polymers with a greater range of composition could be obtained if phenothiazine was included in the polymerization mixture. Within the series, the elongation at break varied for most of the samples between 66 and 175%. A number of tensile strengths in excess of 600 psi was obtained with a few exceeding 700 psi.

In this series, several levels of vinyl monomer and several catalyst levels were examined, but no clear pattern could be observed in the effects of the different variables, except that markedly lower elongations at break were obtained at the 5% vinyl level.

One sample, after being cured, was stored in a vessel at 94°C containing saturated water vapor for 7 days before it was postcured. This sample had the highest tensile strength of any of those tested, showing, at the very least, that the polymer had not been subjected to any significant hydrolytic degradation.

6. Variations in tensile strengths and percent elongations: An effort was made to improve the tensile strength properties of the experimental elastomers through examining the effects of molecular weight, polymer structure, and compounding variables on tensile strength and percent elongation. Conditions were ultimately found for which tensile strengths in the 600-800 psi range could reliably be obtained, but values greater than that range were not achieved. Depending on conditions, elongations in the range of 50-150% were obtained.

Since the first polymers had relatively low molecular weights, it was felt that improvements in the molecular weight would provide improved tensile strengths. The data in Table I provide a summary of the properties of a number of elastomers that were prepared both from the lower molecular weight polymers and from the polymers which were prepared after techniques were developed to increase the molecular weights. The data also represent two levels of vinyl monomer in the composition and two catalyst levels.

At a low vinyl content, low molecular weights reduce strength, and at high vinyl content and high catalyst level, high molecular weights reduce strength. The latter results can probably be attributed in some instances to overmilling of the tough polymers or failure to achieve good mixing during the milling. The optimum milling was difficult to achieve with the higher molecular weight polymers and care taken to avoid overshearing may have led to incomplete mixing. As the work progressed, heated rollers were used to reduce the bulk viscosity of the polymer. It is interesting that some of the highest strength elastomers were obtained from relatively low molecular weight polymers when the vinyl monomer and catalyst levels were sufficiently high.

More detailed information on the relationship of vinyl content and catalyst level is summarized in Table II. For this table, the highest value (an average of three determinations) for tensile strength along with the corresponding percent elongation was selected when replicate values for different samples of the same composite were available. The higher values are perhaps more reliable since an average would be more influenced

TABLE I

VARIATION OF TENSILE STRENGTH AND PERCENT ELONGATION OF EXPERIMENTAL ELASTOMERS WITH POLYMER INHERENT VISCOSITY AT SEVERAL LEVELS OF PERCENT p-PHENYLENEBIS(METHYLVINYLSILANOL) AND CATALYST IN THE COMPOSITION

All polymers prepared from decamethyl-5-dioxa-3,7-diaza-2,4,6,8-tetrasilacyclooctane, oxydi-p-phenylenebis(dimethylsilanol); milled with 40 parts of Hi Sil 233, the specified parts of tert-butyl peroxybenzoate, and no Mapico Red; and cured at 300°F

1.7 Parts of Catalyst

2 Mole % of p-Phenylenebis(methylvinylsilanol)			4-5 Mole % of p-Phenylenebis(methylvinylsilanol)		
η_{inh} (dl/g)	Tensile (psi)	Elongation (%)	η_{inh} (dl/g)	Tensile (psi)	Elongation (%)
0.38	561	91	0.35	690	80
0.38	429	85	0.36	697	73
0.40	608	101	0.48	683	54
1.05	729	123	0.54	600	72
1.13	648	107	1.55	739	96
1.82	670	95	2.07	729	79
Average	608	101	Average	690	75

3.0 Parts of Catalyst

2 Mole % of p-Phenylenebis(methylvinylsilanol)			4-5 Mole % of p-Phenylenebis(methylvinylsilanol)		
η_{inh} (dl/g)	Tensile (psi)	Elongation (%)	η_{inh} (dl/g)	Tensile (psi)	Elongation (%)
0.38	320	52	0.35	748	67
0.38	341	59	0.36	775	71
0.40	610	94	0.54	150	33
1.05	636	110	1.55	549	52
1.13	392	60	2.07	313	33
Average	460	75	Average	507	51

TABLE II

VARIATION OF TENSILE STRENGTH AND PERCENT ELONGATION OF EXPERIMENTAL ELASTOMERS WITH PERCENT p-PHENYLENEBIS(METHYLVINYLSILANOL) AND CATALYST IN THE COMPOSITION

All polymers prepared from decamethyl-1,5-dioxa-3,7-diaza-2,4,6,8-tetrasilacycloocatane and oxydi-p-phenylenebis(dimethylsilanol); milled with 40 parts of Hi Sil 233, the specified parts of tert-butyl peroxybenzoate, and no Mapico Red; and cured at 300°F

Heptamethyl-1,3-dioxa-5-aza-2,4,6-trisilacyclohexane						
p-Phenylenebis-	0.6 Parts Catalyst		1.7 Parts Catalyst		3.0 Parts Catalyst	
(methylvinylsilanol)	Tensile	Elongation	Tensile	Elongation	Tensile	Elongation
(mole %)	(psi)	(%)	(psi)	(%)	(psi)	(%)
1	430	144	670	230	610	175
2	390	92	550	131	550	135
4-5	680	93	710	66	635	77

Decamethyl-1,5-dioxa-3,7-diaza-2,4,6,8-tetrasilacyclooctane						
p-Phenylenebis-	0.6 Parts Catalyst		1.7 Parts Catalyst		3.0 Parts Catalyst	
(methylvinylsilanol)	Tensile	Elongation	Tensile	Elongation	Tensile	Elongation
(mole %)	(psi)	(%)	(psi)	(%)	(psi)	(%)
2	630	123	729	123	636	110
4-5	510	78	739	96	775	71
8			685	61		

by specimens containing flaws. The tabulation shows clearly the expected result that higher vinyl levels decrease the percent elongation. The same effect is observable, but less pronounced for higher catalyst levels. On the basis of these results, most of the subsequent samples examined were based on a vinyl content of 4-5% and a catalyst level of 1.7 parts.

Because milling appeared to be a problem in obtaining high strength elastomers, filler level in the cured elastomers from a high molecular weight polymer was examined as a function of strength (Table III). Of the proportions of filler tried, at least 40 parts was required to achieve strengths comparable to those in Tables I and II.

Most other variables in the polymer composition caused little effect on strength and elongation properties. The exception was that higher strength elastomers were obtained from compositions prepared from oxydi-p-phenylenebis(dimethylsilanol) than from those prepared from p-phenylenebis(dimethylsilanol), although a great deal less work was done in optimizing the latter system. Data comparing compositions based on the various cyclosiloxazanes and the two arylenedisilanols with and without Mapico Red and cured at different temperatures are summarized in Table IV. Again in this table, highest values from replicate samples were used.

7. Reversion: A desirable property for high temperature elastomers is that they retain their strength properties after being heated under autogenous pressure in a closed system at 250°C for 24 hr. The particular system under study in this work offers the possibility of withstanding these conditions because only short siloxane segments are present in the chain, a situation that would limit the probability of decomposition through cyclization. As a consequence, this property was studied in some detail. The results are summarized in Table V.

The effect of polymer structure and composition on stability under these conditions is marked. At the 2 mole % level, p-phenylenebis(methylvinylsilanol) did not contribute as much to the stability as it did when 4 or 8 mole % of the co-monomer was present. Monomers that provided links with more than four silicon atoms between arylene groups were less stable. The remarkably high strength retention of 72% was obtained for the polymer prepared from p-phenylenebis(dimethylsilanol) and decamethyl-1,5-dioxa-3,7-diaza-2,4,6,8-tetrasilacyclooctane.

8. Thermal stability: Under conditions of isothermal air aging, elastomers of various compositions lost about 25% of their weight within 70 hr at 340°C and became brittle. When the temperature was lowered to 300°C, a similar extent of decomposition was observed at 170 hr. At a still lower temperature, weight losses were slower and about 15% of the original polymer weight had been lost after 670 hr.

TABLE III

VARIATION OF TENSILE STRENGTH AND PERCENT ELONGATION OF EXPERIMENTAL ELASTOMERS WITH FILLER LEVEL IN THE COMPOSITION

All polymers prepared from decamethyl-1,5-dioxa-3,7-diaza-2,4,6,8-tetrasilacyclooctane and oxydi-p-phenylenebis(dimethylsilanol) with 2 mole % p-phenylenebis(methylvinylsilanol); milled with the specified parts of Hi Sil 233, Mapico Red, and 1.7 parts of tert-butyl peroxybenzoate; and cured at 300°F

Hi Sil 233 (parts)	Mapico Red (parts)	Tensile (psi)	Elongation (%)
5	0	121	126
10	0	116	109
20	0	216	104
40	0	606	104
40	3	752	100
50	3	708	80
70	3	795	43

TABLE IV

VARIATION IN TENSILE STRENGTHS AND PERCENT ELONGATION OF EXPERIMENTAL ELASTOMERS BASED ON VARIOUS CYCLOSILOXAZANE AND ARYLENEDISILANOLS, WITH AND WITHOUT MAPICO RED AND CURED AT DIFFERENT TEMPERATURES

All polymers prepared from decamethyl-1,5-dioxa-3,7-diaza-2,4,6,8-tetrasilacyclooctane and oxydi-p-phenylenebis(dimethylsilanol) with 2 or 4-5 mole % of p-phenylenebis-(methylvinylsilanol); milled with 40 parts of Hi Sil 233, 3 parts of Mapico Red, and 1.7 parts of tert-butyl peroxybenzoate; and cured at 300°F, unless otherwise specified.

	p-Phenylenebis(methylvinylsilanol)			
	2 Mole %		4-5 Mole %	
	Tensile (psi)	Elongation (%)	Tensile (psi)	Elongation (%)
Cyclosiloxazane				
$(CH_3)_{10}Si_4N_2O_2$	729	103	739	96
$(CH_3)_7Si_3NO_2$	550	131	710	66
$(CH_3)_9Si_4NO_3$	--	--	609	84
Arylenedisilanol				
$O[C_6H_4\text{-}p\text{-}Si(CH_3)_2OH]_2$	729	103	739	106
$p\text{-}C_6H_4[Si(CH_3)_2OH]_2$	573	51	549	44
Mapico Red (parts)				
0	729	123	739	96
3	752	100	675	64
Cure Temperature (°F)				
300	729	103	739	106
280	788	107	724	66

TABLE V

EFFECT OF HEATING EXPERIMENTAL ELASTOMERS AT 250°C IN A CLOSED SYSTEM ON THEIR TENSILE STRENGTHS AND PERCENT ELONGATIONS

All polymers prepared from decamethyl-1,5-dioxa-3,7-diaza-2,4,6,8-tetrasilacyclooctane and oxydi-p-phenylenebis(dimethylsilanol) with 4 mole % of p-phenylenebis(methylvinylsilanol); milled with 40 parts of Hi Sil 233, 3 parts of Mapico Red, and 1.7 parts of tert-butyl peroxybenzoate; and cured at 300°F, unless otherwise specified.

Mapico Red (parts)	p-Phenylenebis(methylvinylsilanol) (mole %)	Postcured		Heated at 250°C for 24 Hr in a Closed Container		Strength Retention (%)
		Tensile (psi)	Elongation (%)	Tensile (psi)	Elongation (%)	
0	2	606	104	126	141	21
0	4	683	54	248	63	36
0	8	685	61	217	73	32
3	2	788	107	142	123	18
3	4	728	69	305	72	42
Mapico Red (parts)	**Cyclosiloxazane**					
0	$(CH_3)_{10}Si_4N_2O_2$	683	54	248	63	36
0	$(CH_3)_7Si_3NO_2$	664	88	99	84	15
0	$(CH_3)_9Si_4NO_3$	609	84	88	117	14
Arlyenedisilanol						
$O[C_6H_4\text{-}p\text{-}Si(CH_3)_2OH]_2$		728	69	305	72	42
$p\text{-}C_6H_4[Si(CH_3)_2OH]_2$		549	44	393	52	72

Most compositional parameters (vinyl content, cyclosiloxazane precursor, and the presence or absence of ferric oxide) has little effect on the weight losses. Polymers based on p-phenylenebis(dimethylsilanol) lost weight somewhat more slowly than those based on oxydi-p-phenylenebis-(dimethylsilanol).

The effect was better documented by aging tensile test specimens in a circulating air oven at 260°C. Whereas a polymer based on p-phenylenebis-(dimethylsilanol) retained 97% of its strength after 100 hr, 84% after 300 hr, and 78% after 500 hr, a similar polymer based on oxydi-p-phenylenebis(dimethylsilanol) retained only 75% of its strength after 100 hr, 36% after 300 hr, and 58% after 500 hr.

In order to better assess the nature of the decomposition that was occurring, a series of thermogravimetric experiments was carried out in which the polymers were heated at various heating rates, both in air and in nitrogen. Marked differences in thermogravimetric heat stabilities were obtained depending on the particular conditions. The data, however, continued to show that the polymers with the oxydi-p-phenylene group were more stable than those containing the p-phenylene groups, which is difficult to reconcile with the isothermal data.

These data were further treated to show that air oxidation remains an important factor, even at 260°C, in polymers with methyl groups pendant to siloxane chains. Activation energies for decomposition were calculated from these data according to the method of Flynn and Wall (Ref. 2) and found to be 19.2 kcal/mole for the polymer containing the oxydi-p-phenylene group and 16.1 kcal/mole for the polymer containing the p-phenylene group when these polymers were heated in air. Doyle has reported that the net apparent activation energy for the oxidation of a silicone resin in air was 22.2 kcal/mole (Ref. 3), a value not greatly different from those found here. It can therefore be assumed that the primary event in the decomposition of these elastomers in air is oxidation rather than thermal depolymerization. The data obtained in this work were not adequate to determine if the calculated activation energies for the decomposition in nitrogen represented thermal depolymerization, which is about 43 kcal/mole (Ref. 4).

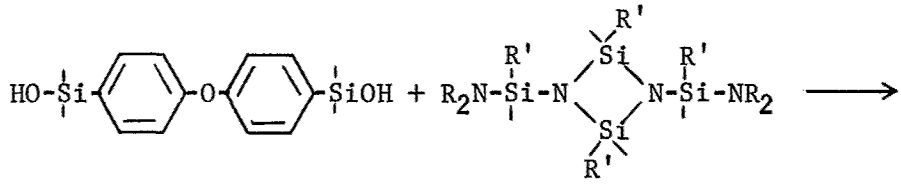
The thermogravimetric data for polymers prepared from decamethyl-1,5-dioxa-3,7-diaza-2,4,6,8-tetrasilacyclooctane, oxydi-p-phenylenebis(dimethylsilanol) or p-phenylenebis(dimethylsilanol), and 4 mole % of p-phenylenebis-(methylvinylsilanol) are summarized in Figures 1-5.*

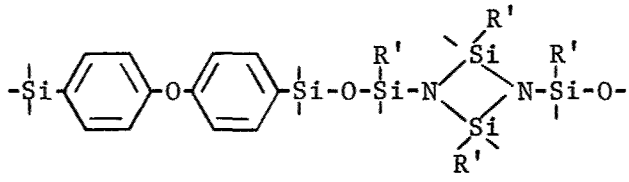
9. Hydrolytic stability and low temperature properties: Strength losses of 35-55% were observed after samples were stores at 65-95°C for 500 hr under sufficiently moist conditions that there was continual condensation of water in the samples.

* All figures appear at the end of the report.

Brittle temperatures were determined for several compositions. A value of -100°C was obtained for the condensate from p-phenylenebis(dimethylsilanol) and decamethyl-1,5-dioxa-3,7-diaza-2,4,6,8-tetrasilacyclohexane. The polymer from the same cyclosiloxazane and oxydi-p-phenylenebis(dimethylsilanol) has a brittle point of -70°C but the temperature could be lowered through the use of compositions based on cyclosiloxazanes providing longer siloxane chain segments.

B. Condensation Polymers From Arylenedisilanols and Cyclodisilazane Derivatives





R = CH_2
= C_2H_5
R' = CH_3
= $CH_2CH_2CF_3$

One series of polymers was prepared from oxydi-p-phenylenebis(dimethylsilanol) and N,N'-bis[(diethylamino)dimethylsilyl]tetramethylcyclodisilazane and each polymer was milled with filler and catalyst. These polymers did not cure at 300°F unless 2 mole % of p-phenylenebis(methylvinylsilanol) was present in the composition. The cured polymers had low strengths (less than 150 psi), and since condensates from these polymers are known to be hydrolytically unstable, the work was not pursued further.

Of considerably more interest were condensates of oxydi-p-phenylenebis(dimethylsilanol) and N,N'bis[(dimethylamino)methyl-3,3,3-trifluoropropylsilyl]-2,4-bis(3,3,3-trifluoropropyl)-2,4-dimethylcyclodisilazane, which are more hydrolytically stable. A polymer of this composition was used in a hydrolytic stability screening in which the infrared spectra of a thin film on a KRS-5 optic was compared with spectra of a similar film of the permethyl polymer at 200°F under conditions of high humidity. The permethyl polymer was nearly completely decomposed after 1 day's exposure, but the film of the fluorine-substituted polymer was stable for at least 4 days. Stability was determined by comparing the relative intensities of the silicon-methyl band at about 1260 cm^{-1} and the cyclodisilazane band at about 1010 cm^{-1}. Either leaching occurred or the polymer underwent gravity flow during the test with a consequent thinning and weakening of all absorption

peaks. Presumably, if the molecular weight of this condensate could be increased, the problem of the thinning of the film could be avoided.

The work on this polymer system was delayed owing to apparent problems in purity, which are discussed in Paragraph II.C.2. Two very low molecular weight polymers (η = 0.06 and 0.09 dl/g) based on these monomers with 5 mole % of p-phenylenebis(methylvinylsilanol) were prepared, but neither could be cured with tert-butyl peroxybenzoate at 300°F. An attempt to advance the polymerization thermally with phenothiazine added to the mixture led to the loss of solubility of the polymer in toluene.

C. Synthesis of Monomers and Intermediates

A considerable effort was devoted to the synthesis and purification of larger quantities of monomers for use in polymer preparations in the screening of the materials as elastomers. Although all of the necessary procedures had been carried out previously, it was necessary in some instances to modify or improve the methods.

1. Arylenedisilanol and cyclosiloxazane monomers and their intermediates: Although the procedure for the preparation of p-phenylenebis(dimethylsilanol) and p-phenylenebis(methylvinylsilanol) and the intermediates p-phenylenebis(ethoxydimethylsilane), oxydi-p-phenylenebis(ethoxydimethylsilane), and p-phenylenebis(ethoxymethylvinylsilane), were straightforward and offered no difficulties, products of inconsistent quality were obtained in the preparation of oxydi-p-phenylenebis(dimethylsilanol). The problem of purity of this monomer in relationship to polymer synthesis was discussed in Paragraph IV.A.1.

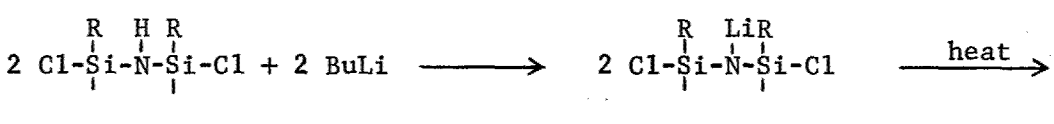
The best means to insure satisfactory purity was to dry samples of oxydi-p-phenylenebis(dimethylsilanol) at 70°C under vacuum until their differential thermal analysis traces showed no endotherms or exotherms prior to fusion. Samples in which such effects persisted on continued heating and in which the fusion endotherm broadened were redissolved in ethanol as their sodium salts and rehydrolyzed. The behavior on differential thermal analysis appears to be the best criterion for the suitability of these compounds in polymerization reactions.

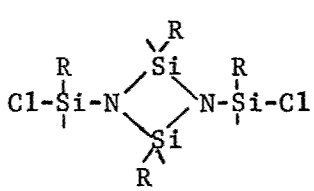
The cyclosiloxazanes were purified by distillation on a spinning-band column, and careful distillations were required to obtain products with high purity according to g.l.c. Decamethyl-1,5-dioxa-3,7-diaza-2,4,6,8-tetrasilacyclooctane was particularly difficult to obtain in high purity

since it contained an impurity that boiled within several degrees of the cyclosiloxazane. Few of the monomers were obtained as 100% pure materials, and although the impurities seemed to promote vinyl polymerization of the p-phenylenebis(methylvinylsilanol) co-monomer in the polycondensation reactions, the effect could be minimized when inhibitors were present in the mixtures.

Although the proportion of products in the preparation of α,ω-dichlorosiloxane precursors for the synthesis of the cyclosiloxazanes vary from preparation to preparation, a sufficient number of experiments has been carried out to indicate that the distribution to be expected is about 15:30:15% yield of 1,3-dichlorotetramethyldisiloxane, 1,5-dichlorohexamethyltrisiloxane, and 1,7-dichlorooctamethyltetrasiloxane, respectively, under the experimental conditions. Yields varied from experiment to experiment owing to the failure to exactly reproduce distillation conditions. Redistribution of functional groups may continue to occur during distillation as long as the ferric chloride catalyst is present in the mixture.

2. Cyclodisilazane monomers and intermediates: N,N'-Bis(chlorodimethylsilyl)tetramethylcyclodisilazane was obtained in excellent yield by heating the lithium salt prepared from 1,3-dichlorotetramethyldisilazane and butyllithium. By-products, normally present in the equilibration of dichlorodimethylsilane and hexamethylcyclotrisilazanes to obtain the same product, were not produced in this condensation. During this reporting period, the method has been extended to include the synthesis of N,N'-bis-(chloromethylphenylsilyl)-2,4-dimethyl-2,4-diphenylcyclodisilazane from 1,3-dichloro-1,3-dimethyl-1,3-diphenyldisilazane; N,N'-bis(chloroethylmethylsilyl)-2,4-diethyl-2,4-dimethylcyclodisilazane from 1,3-dichloro-1,3-diethyl-1,3-dimethyldisilazane; and N,N'-bis(chloromethyl-3,3,3-trifluoropropylsilyl)-2,4-bis(3,3,3-trifluoropropyl)-2,4-dimethylcyclodisilazane from 1,3-bis(3,3,3-trifluoropropyl)-1,3-dichloro-1,3-dimethyldisilazane.





R = C_6H_5
= C_2H_5
= $CH_2CH_2CF_3$

The modified synthesis procedure has been of particular interest for cyclodisilazane derivatives substituted with 3,3,3-trifluoropropyl groups because condensation polymers of arylenedisilanols with 3,3,3-trifluoropropyl-substituted cyclodisilazane show a marked improvement in hydrolytic

stability over those prepared from the permethyl derivatives. Although a cyclodisilazane derivative could be prepared by the equilibration procedure, the conversion was not high. Elemental analysis data appeared to be satisfactory, but the product showed multiple peaks on g.l.c. Because the equilbration procedure is known to produce a number of by-products, the multiple g.l.c. peaks could not be attributed with certainty to possible structural isomerism.

In several preparations of N,N'-bis[chloro(methyl)-3,3,3-trifluoropropylsilyl]-2,4-bis(3,3,3-trifluoropropyl)-2,4-dimethylcyclodisilazane by the butyllithium procedure, conversions of about 70% were obtained. The product was fractionally distilled three times, but products from each of the successive distillations showed multiple g.l.c. peaks and little enrichment of the chief component. When these intermediates were converted to the dimethylamino monomers, some of the products, which were solid-liquid mixtures, showed the presence of Si_2NH absorption in their infrared spectra even though such an absorption was absent in the chlorine-substituted intermediate. One of the dimethylamino derivatives was washed with petroleum ether to give a 20% recovery of a material melting at 101-106° and provided an excellent elemental analysis for N,N'-bis[(dimethylamino)methyl-3,3,3-trifluoropropyl]-2,4-bis-(3,3,3-trifluoropropyl)2,4-dimethylcyclodisilazane. This material also showed multiple g.l.c. peaks.

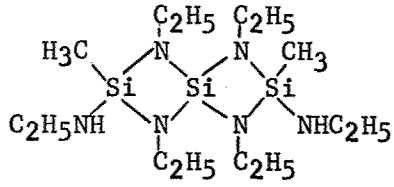
It is therefore necessary to attribute the multiple g.l.c. peaks and wide melting ranges for these compounds to the existence of isomers. This possibility had at first been discounted because, unlike the phenyl-substituted cyclodisilazane derivatives which form isomers, the methylsilyl proton absorption occurred as a single peak in the n.m.r. spectra. If the presence of isomers must be assumed, it is difficult to establish criteria for purity for the monomers other than the elemental analyses.

D. Other Preparations

A 248-g sample of 1,1,1-trichloro-3,3,3-trimethyldisilazane was prepared by treating hexamethyldisilazane with silicon tetrachloride and forwarded to the Materials Laboratory. Immediately after its preparation and purification, the substance was g.l.c. pure, but after 3 weeks' storage an impurity could be detected in the material. It is possible that disproportionation could occur in such a structure, and if pure material is required, it may need to be freshly distilled just prior to use.

In an attempt to prepare 1,1-dichloro-1,3,3,3-tetramethyldisilazane from hexamethyldisilazane and methyltrichlorosilane, disproportionation of the product did occur during the distillation and a considerable amount of solid, but unidentified product, was obtained.

A new difunctional silazane monomer was prepared by sequentially treating one equivalent of methyltris(ethylamino)silane with two equivalents of butyllithium and one equivalent of silicon tetrachloride. The monomer, 2,5-bis(ethylamino)-2,5-dimethyl-1,3,4,6-tetraethylspiro[3.3]-trisilazane, has been characterized.



III.

SUMMARY

A. A procedure was developed by which adequate p-phenylenebis(methylvinylsilanol) could be incorporated in cyclosiloxane-arylenedisilanol polymers to provide crosslinking sites for curing. By this method, in which phenothiazine was added to the polymerizing mixture, polymers with inherent viscosities up to 3.5 dl/g were obtained.

B. Oxydi-p-phenylenebis(dimethylsilanol)-cyclosiloxazane condensates could reproducibly be prepared, compounded, and cured to elastomers with tensile strengths at break in the range of 600-800 psi and elongation at break of 50-150%. Depending on the cyclosiloxazane, these elastomers retained up to 40% of their strength after 24 hr in a closed vessel at 250°C. Best stabilities were obtained when the polymers were prepared from decamethyl-1,5-dioxa-3,7-diaza-2,4,6,8-tetrasilacyclooctane. The polymers retained 58% of their strength after 500 hr in a circulating air oven at 260°C.

C. A p-phenylenebis(dimethylsilanol)-decamethyl-1,5-dioxa-3,7-diaza-2,4,6,8-tetrasilacyclooctane condensate containing 4 mole % of p-phenylenebis(methylvinylsilanol), with a tensile strength of 549 psi and a 44% elongation at break, retained 72% of its strength after 24 hr and in a closed vessel at 250°C and retained 78% of its strength after 500 hr in a circulating air oven at 260°C. This polymer had a brittle temperature of -100°C.

D. Although the polymers from p-phenylenebis(dimethylsilanol) were more stable than the polymers from oxydi-p-phenylenebis(dimethylsilanol) under conditions of isothermal aging, the latter continued to appear to be more stable on thermogravimetric analyses. Calculation of activation energies of decomposition indicate that the primary decomposition event in air is methyl group oxidation and not depolymerization with the formation of cyclic structures.

E. Compounded and cured polymers from oxydi-p-phenylenebis(dimethylsilanol) and N,N'-bis[dimethyl(dimethylamino)silyl]tetramethylcyclodisilazane with p-phenylenebis(methylvinylsilanol) had tensile strengths at break below 150 psi. The corresponding polymers from N,N'-bis[(dimethylamino)methyl-3,3,3-trifluoropropylsilyl]-2,4-bis(3,3,3-trifluoropropyl)-2,4-dimethylcyclodisilazane could not be cured. The improved hydrolytic stability of the latter polymer was established.

F. Improved synthetic procedures were established for N,N'-bis[(dimethylamino)methyl-3,3,3-trifluoropropylsilyl]-2,4-bis(3,3,3-trifluoropropyl)-2,4-dimethylcyclodisilazane, N,N'-bis[chloro(ethyl)methylsilyl]-2,4-diethyl-2,4-dimethylcyclodisilazane, and N,N'-bis[chloro(methyl)phenylsilyl]-2,4-dimethyl-2,4-diphenylcyclodisilazane. The procedure involves the thermolysis of the lithium salts of 1,3-dichloro-1,3-diorgano-1,3-dimethyldisilazanes.

G. A new difunctional spirosilazane monomer, 2,5-bis(ethylamino)-2,5-dimethyl-1,3,4,6-tetraethylspiro[3,3]trisilazane, was prepared and characterized.

IV.

EXPERIMENTAL

All chlorosilanes were redistilled before being used. Reactions with hydrolytically sensitive compounds were carried out in glass equipment that had been flame-dried and flushed with dry nitrogen before use. Reactants were protected from atmospheric moisture with Drierite-packed tubes or a positive pressure of dry nitrogen as needed. Elemental analyses were conducted by Spang Microanalytical Laboratory. Infrared spectra were determined with a Perkin-Elmer Infracord spectrophotometer and n.m.r. spectra were determined with a Varian Associates Model A60 spectrometer using cyclohexane as an internal standard. The inherent viscosities of polymers were determined in toluene solution at 30°C in a concentration of 0.5%.

A. Synthesis of Arylenedisilanol Monomers and Intermediates

1. p-Phenylenebis(ethoxydimethylsilane): A solution of 354 g (1.49 moles) of freshly recrystallized p-dibromobenzene in 775 ml dry tetrahydrofuran was added in rapid drops to 80.2 g (3.30 g-atoms) of previously activated magnesium covered with 50 ml of tetrahydrofuran. The reaction proceeded exothermally. After the addition was complete, the mixture was refluxed for 2 hr, then treated with 444 g (3.00 moles) of diethoxydimethylsilane in rapid drops. An additional exothermic reaction occurred during the addition. The product was refluxed overnight, cooled to room temperature, and filtered to remove the unchanged magnesium. Magnesium salts were precipitated by concentration of the filtrate on a rotary evaporator and extracted exhaustively with petroleum ether, b.p., 60-90°C. The combined extracts were combined, concentrated, and distilled. Redistillation on a 36-in. spinning band column gave 193 g (46%) of p-phenylenebis(ethoxydimethylsilane), b.p. 117-118°C (3.5 mm), n_D^{20} 1.4790-1.4792 [reported b.p., 119-120°C (3.6 mm), n_D^{20} 1.4782] (Ref. 5).

2. p-Phenylenebis(dimethylsilanol): A total of 193 g (0.684 mole) of p-phenylenebis(ethoxydimethylsilane) was added to a solution of 142 g (3.55 moles) of sodium hydroxide in 500 ml of methanol and 56 ml of water. To this mixture was added a solution of 142 g (3.55 moles) of sodium hydroxide in 550 ml of water. After 1 hr, the solution was added to a rapidly stirred mixture of 2.8 kg of ice, 2.8 kg of water and 724 g (5.32 moles) of monobasic sodium phosphate. The precipitated compound was filtered off, washed with water until the washings were neutral, and recrystallized twice from toluene. There was obtained 129 g (83%) of p-phenylenebis(dimethylsilanol), m.p. 135-136°C (reported, 136-137°C) (Ref. 5).

3. Diethoxymethylvinylsilane: A solution of 298 g (6.47 moles) of dry ethanol in 484 g (6.12 moles) of pyridine was added dropwise to a solution of 432 g (3.06 moles) of dichloromethylvinylsilane in 2 liters of petroleum ether, b.p. 35-60°C, while the temperature was maintained between 15-20°C with an ice bath. After the mixture was stored overnight, filtration gave 713 g (calcd. 710 g) of pyridine hydrochloride. Concentration of the filtrate and fractional distillation gave 345 g (70%) of diethoxymethylvinylsilane, b.p. 132-133°C, n_D^{20} 1.4007 (reported b.p. 132°C, n_D^{20} 1.4006) (Ref. 1b).

4. p-Phenylenebis(ethoxymethylvinylsilane): A solution of 255 g (1.08 moles) of p-dibromobenzene in 550 ml of tetrahydrofuran was added in rapid drops to 56.1 g (2.31 g-atoms) of previously activated magnesium covered with 20 ml of tetrahydrofuran at a rate that maintained rapid reflux. After the addition was complete, heating was continued for 2 hr and 345 g (2.16 moles) of diethoxymethylvinylsilane was added. The mixture was refluxed overnight, cooled, and filtered to remove 4.8 g of unchanged magnesium. After the magnesium salts were precipitated by evaporation of the solvent the residue was extracted exhaustively with petroleum ether, b.p. 60-90°C. Evaporation of the solvent and distillation of the product gave 190 g of crude product which, upon fractional distillation on a 36-in. spinning-band column, gave 154 g (49%) of p-phenylenebis(ethoxymethylvinylsilane), b.p. 107°C (0.5 mm), n_D^{20} 1.4960 [reported b.p. 140°C (2 mm)] (Ref. 1b).

5. p-Phenylenebis(methylvinylsilanol): A solution of 154 g (0.505 mole) of p-phenylenebis(ethoxymethylvinylsilane) in 150 ml of 95% ethanol was treated sequentially with a solution of 104 g (2.55 moles) of sodium hydroxide in 355 ml of methanol and 33 ml of water and a solution of 104 g (2.55 moles) of sodium hydroxide in 388 ml of water. After 1 hr, this solution was added dropwise with rapid stirring to a mixture of 526 g (3.87 moles) of monobasic potassium phosphate, 2 kg of ice, and 2 kg of water. The precipitated solids were filtered off, washed exhaustively with water, and dried under vacuum. Recrystallization from toluene gave 91 g (71%) of p-phenylenebis(methylvinylsilanol), m.p. 95-96°C (capillary) [reported m.p., 95-96°C (differential thermal analysis)] (Ref. 1b).

6. Oxydi-p-phenylenebis(ethoxydimethylsilane): To 115 g (4.71 g-atoms) of freshly activated magnesium covered with 200 ml of tetrahydrofuran was added a solution of 700 g (2.14 moles) of p-bromophenyl ether in 1.1 liters of tetrahydrofuran over a period of 2.5 hr at a rate that maintained a brisk reflux. Heating was continued for 2 hr, then 634 g (4.28 moles) of diethoxydimethylsilane was added in 1 hr and heating was continued overnight. The cooled mixture was filtered to remove 13.5 g of unchanged magnesium and evaporated on a rotary evaporator to precipitate the magnesium salts. The residue was extracted three times with an excess of petroleum ether,

b.p. 60-90°C, the second extraction preceded by passing the salts through a No. 6 mesh screen and the third extraction preceded by passing the salts through a No. 14 mesh screen. After the extracts were evaporated and the residue was flash distilled, 535 g of crude oxydi-p-phenylenebis(ethoxydimethylsilane) was obtained. In an attempt to purify this batch by distillation, the material was lost through the breakage of the distillation pot.

The procedure was repeated in a second experiment and 595 g of the impure oxydi-p-phenylenebis(ethoxydimethylsilane) was obtained after the preliminary distillation. Fractional distillation on a 36-in. spinning-band column gave 462 g (58%) of oxydi-p-phenylenebis(ethoxydimethylsilane), b.p. 144-146°C (0.1 mm), n_D^{20} 1.5200 [reported b.p. 137-138°C (0.01 mm)], n_D^{20} 1.5210 (Ref. 1c).

In another repetition of the procedure with 1.94 moles of bis(p-bromophenyl)ether, 52% of oxydi-p-phenylenebis(ethoxydimethylsilane), b.p. 144°C (0.04 mm), n_D^{20} 1.5200-1.5208 was obtained.

7. Oxydi-p-phenylenebis(dimethylsilanol): In two batches, 231 g (0.62 mole) of oxydi-p-phenylenebis(ethoxydimethylsilane) was added to a solution of 126 g (3.1 moles) of sodium hydroxide in 442 ml of methanol and 50 ml of water and then a solution of 126 g (3.1 moles) of sodium hydroxide in 500 ml of water was added. Stirring was continued for 3 hr. The solution was added dropwise to a rapidly stirred mixture containing 315 g (2.3 moles) of monobasic potassium phosphate, 2.2 liters of water, and 2.2 kg of ice. After the precipitated silanol was washed thoroughly by sequentially slurrying the solids with distilled water and filtering off the insoluble portion until the washings were neutral, the silanol was dried at 55°C for 24 hr under vacuum. Two recrystallizations from toluene-petroleum ether mixtures gave, after the product was dried for 48 hr at 70°C under vacuum, in one experiment 136 g (70%) and in the other 128 g (65%) of oxydi-p-phenylenebis(dimethylsilanol), m.p. 101-103°C and 101-103°C. Differential thermal analysis showed that neither sample was pure.

The foregoing samples were reworked in the following manner: A 133-g (0.42 mole) portion of oxydi-p-phenylenebis(dimethylsilanol) was redissolved in a sodium hydroxide solution and precipitated from a solution of monobasic potassium phosphate. The oxydi-p-phenylenebis(dimethylsilanol) was added to a solution of 83.6 g (2.1 moles) of sodium hydroxide in 293 ml of methanol and 34 ml of water and a solution of 83.6 g (2.1 moles) of sodium hydroxide in 326 ml of water was subsequently added to the mixture. After the mixture was heated to boiling over a 2-hr period, 6.5 g of a waxy solid was removed. The remaining solution was cooled and added slowly to a stirred mixture of 433 g (3.1 moles) of monobasic potassium phosphate, 1,650 ml of water, and 1,650 g of crushed ice. After the precipitated

material was filtered off and washed with distilled water until the washings were neutral, two recrystallizations from 200 ml of toluene gave 92 g (69% recovery) of oxydi-p-phenylenebis(dimethylsilanol), m.p. 103-105°C (reported m.p. 103-104°C) (Ref. 5). The second portion of oxydi-p-phenylenebis(dimethylsilanol), dissolved in 200 ml of 95% ethanol rather than being added undiluted to the saponifying mixture, gave 121 g (91% recovery) of oxydi-p-phenylenebis(dimethylsilanol), m.p. 102-104°C was obtained.

A total of 119 g (0.375 mole) of very impure oxydi-p-phenylenebis(dimethylsilanol) recovered from various recrystallization liquors was heated in a mixture of 1 liter of 95% ethanol and 105.6 g (1.88 moles) of potassium hydroxide until the diol had dissolved. A heating period of 0.5 hr under reflux was necessary. The cooled solution was added dropwise to a stirred mixture of 194 g (1.43 moles) of monobasic potassium phosphate in 1.4 liters of water and 1.4 kg of ice. The gummy precipitate was filtered off, washed exhaustively with water, air dried, recrystallized twice from 200-ml portions of toluene, and dried overnight at 70°C under vacuum. The product, 52 g (44% recovery) was not completely pure after two recrystallizations from toluene.

Subsequently, 49.3 g (0.155 mole) of this impure oxydi-p-phenylenebis(dimethylsilanol) dissolved in 75 ml of 95% ethanol, was added to a solution of 31.2 g (0.78 mole) of sodium hydroxide in 110 ml of methanol and 12 ml of water. The mixture was treated with a solution of 31.2 g (0.78 mole) of sodium hydroxide in 122 ml of water and stirred for 3 hr at room temperature. The solution was then added dropwise to a rapidly stirred mixture of 160 g (1.18 moles) of monobasic potassium phosphate in 630 ml of water and 630 g of ice. After the precipitate was filtered off and washed with distilled water until it was neutral, it was dried overnight under vacuum at 70°C. When the product was recrystallized twice from toluene and dried overnight, 40.3 g (82% recovery) of pure oxydi-p-phenylenebis(dimethylsilanol), m.p. 103-104°C (differential thermal analysis), was obtained.

In a similar procedure, 218 g (0.581 mole) of oxydi-p-phenylenebis-(ethoxydimethylsilane), treated first with 116 g (2.91 moles) of sodium hydroxide in 407 ml of methanol and 46 ml of water and second with 116 g (2.91 moles) of sodium hydroxide in 453 ml of water and hydrolyzed with a mixture of 600 g (4.41 moles) of monobasic potassium phosphate in 2.33 liters of water and 2.33 kg of ice, gave 152 g (82%) of pure oxydi-p-phenylenebis(dimethylsilanol), m.p. 103-105°C, after two recrystallizations from toluene.

The same procedure with 175 g (0.467 mole) of oxydi-p-phenylenebis-(dimethylsilanol) and proportionate quantities of the other materials gave 124 g (84%) of impure oxydi-p-phenylenebis(dimethylsilanol). A differential thermal analysis trace showed a weak endotherm followed by an exotherm at about 95°C, somewhat below the fusion temperature.

This impure product was reworked as two 62-g batches by the procedure described in the third paragraph of this section. In both experiments 53 g (86% recovery) of pure oxydi-p-phenylenebis(dimethylsilanol) was obtained. The purity was verified by differential thermal analysis.

Additional impure samples totaling 47.4 g (0.15 mole) were combined, dissolved in 200 ml of 95% ethanol, mixed with a solution of 41.8 g (0.75 mole) of potassium hydroxide in 200 ml of ethanol, and the mixture was refluxed for 1 hr. The solution was cooled and added dropwise to a rapidly stirred solution of 77.0 g (0.57 mole) of monobasic potassium phosphate in 560 ml of water and 560 g of ice. After the precipitated diol was filtered off, washed exhaustively with water, air-dried for 1 day, and dried under vacuum for 4 hr at 70°C, recrystallization of the product from toluene gave 43.4 g (91% recovery) of oxydi-p-phenylenebis(dimethylsilanol), m.p. 105-106°C (differential thermal analysis).

Two samples prepared earlier (Ref. 1a) were analyzed by emission spectroscopy for sodium and phosphorus. The silanol that had been prepared by the hydrolysis of the sodium salt in which sodium hydroxide and monobasic potassium phosphate were present in a mole ratio of 4:1.5 showed 0.058% sodium and 0.05% phosphorus. The sample prepared with the mole ratio of 4:2 showed 0.065% sodium and 0.04% phosphorus.

B. Synthesis of Cyclosiloxazane Monomers and Intermediates

1. 1,3-Dichlorotetramethyldisiloxane, 1,5-dichlorohexamethyltrisiloxane, and 1,7-dichlorooctamethyltetrasiloxane: After a mixture of 296 g (2 moles) of diethoxydimethylsilane, 1,132 g (8.78 moles) of dichlorodimethylsilane, and 3 g of ferric chloride were mixed and heated to 72°C over a period of 6 hr until ethyl chloride was no longer evolved, 541 g of unchanged dichlorodimethylsilane was distilled off at atmospheric pressure. A rapid distillation of the remainder of the material at 35-40 mm gave 434 g of a mixture of products. When this distillate was redistilled at 40 mm through a 12-in. column packed with Berl saddles, the following fractions were collected: (a) 89.1 g b.p. 58°C; (b) 21.1 g, b.p. 62-94°C; (c) 104.3 g, b.p. 95-96°C; (d) 72.9 g, b.p. 97-127°C; and (e) 89.7 g, b.p. 128°C. Redistillation of (b) gave (f) 49.7 g, b.p. 58°C. Fractions (a) and (f) were identified as 1,3-dichlorodisiloxane (139 g, 17%).

In a similar experiment with 296 g (2.00 moles) of diethoxydimethylsilane, 1,072 g (8.33 moles) of dichlorodimethylsilane, and 3.0 g of ferric chloride, 430 g of dichlorodimethylsilane was recovered and 480 g of a mixture of products was obtained in a preliminary distillation. Fractional distillation at 40 mm gave the following: (g) 108 g, b.p. 58°C; (h) 38 g, b.p. 61-95°C; (i) 165 g, 96°C; (j) 25.7 g, b.p. 102-125°C; and (k) 85 g, 127-128°C. Redistillation of (h) at 40 mm gave 21.9 g (l) of distillate, b.p. 58°C. Fractions (g) and (l) were identified as 1,3-dichlorodisiloxane (130 g, 16%).

All other fractions were combined and redistilled. There was obtained 344 g (31%) of 1,3-dichlorohexamethyltrisiloxane, b.p. 96°C (40 mm) and 159 g (15%) of 1,5-dichlorooctamethyltetrasiloxane, b.p. 127-128°C (40 mm).

In a third experiment with 1,132 g (8.78 moles) of dichlorodimethylsilane, 296 g (2.00 moles) of diethoxydimethylsilane, and 3 g of ferric chloride, heated at about 70°C for 5.5 hr, the following products were obtained: Recovered dichlorodimethylsilane, 441 g; 1,3-dichlorotetramethyldisiloxane, 178 g (22%), b.p. 58°C (40 mm); an intermediate fraction, 40 g; 1,5-dichlorohexamethyltrisiloxane, 198 g (36%), b.p. 95-97°C (40 mm); an intermediate fraction, 27 g; and 1,7-dichlorooctamethyltetrasiloxane, 71 g (7%), b.p. 126-128°C (40 mm).

The 1,3-dichlorotetramethyldisiloxane and 1,5-dichlorohexamethyltrisiloxane were each combined with previously prepared samples and redistilled through a 30-cm saddle-packed column. Distillation of a total of 235 g of the dichlorodisiloxane gave 223 g of 1,3-dichlorotetramethyldisiloxane, b.p. 58°C (40 mm), g.l.c. purity 99.1% (2-meter column packed with 5% SF 96 on 100/120 mesh Gas Chrom Q, 102°C, He carrier, flow rate 44 ml/min). When 339 g of the dichlorotrisiloxane was redistilled, 315 g of 1,5-dichlorohexamethyltrisiloxane, b.p. 97°C (40 mm) was recovered, g.l.c. purity 95.4% (same conditions). A third distillation gave 299 g of 1,5-dichlorohexamethyltrisiloxane, b.p. 98-99°C (40 mm), g.l.c. purity 91.7%.

By the same method, 1,132 g (8.78 moles) of dichlorodimethylsilane, 296 g (2.00 moles) of diethoxydimethylsilane, and 3 g of ferric chloride heated at 71°C for about 8 hr, the following products were obtained: Recovered dichlorodimethylsilane, 515 g; 1,3-dichlorotetramethyldisiloxane, 58 g, b.p. 58-59°C (40 mm) [reported b.p., 58-59°C (40 mm)] (Ref. 7); an intermediate fraction, 94 g; 1,5-dichlorohexamethyltrisiloxane, 141 g, b.p. 96-98°C (40 mm) [reported b.p., 94-96°C (40 mm)] (Ref. 7); and 1,7-dichlorooctamethyltetrasiloxane, 77 g, b.p. 126-128°C (40 mm) [reported b.p. 126-128°C (40 mm)] (Ref. 6).

2. Decamethyl-1,5-dioxa-3,7-diaza-2,4,6,8-tetrasilacyclooctane: Five fractions of previously prepared 1,5-dioxa-3,7-diaza-2,4,6,8-tetrasilacyclooctane were combined and redistilled through an annular spinning-band column. The following fractions were collected and their g.l.c. purity determined (2-meter column packed with 5% SF-96 on 100/200 mesh Gas Chrom Q, column temperature 151°C, He carrier, flow rate 37 ml/min): (a) 1.8 g, b.p. 85-91°C (5 mm), 78%; (b) 26.0 g, b.p. 91°C (5 mm), 97%; (c) 27.5 g, b.p. 91°C (5 mm), 99%; and (d) 27.4 g, b.p. 91°C (5 mm), 100%.

In another preparation, 214 g (1.05 moles) of redistilled 1,3-dichlorotetramethyldisiloxane, dissolved in 750 ml of petroleum ether, b.p. 60-90°C, was heated to 50°C and maintained there with periodic cooling while methylamine was passed over the surface of the stirred liquid until there was evidence of the presence of an excess of the amine. After heating was continued for 1.5 hr, the cooled mixture was filtered and 143.3 g (calcd. 142 g) of methylamine hydrochloride was collected. The solvent was removed in a rotary evaporator at 30°C and the residue was flash-distilled to obtain 108.7 g of crude product. Redistillation on a 30-in. spinning-band column gave the following fractions (including their g.l.c purity): (e) 36.9 g, b.p. 87-88°C (5 mm), 88%; (f) 45.9 g, b.p. 91-92°C (5 mm), 94%.

When fractions (b), (c), (e), and (f) were combined and redistilled through the 36-in. spinning-band column, the following cuts were obtained: (g) 5.2 g, b.p. 80-84°C (5 mm); (h) 11.3 g, b.p. 88-90°C (5 mm), 82%; (i) 23.0 g, b.p. 90°C (5 mm), 93%; (j) 20.2 g, b.p. 90°C (5 mm), 95%; and (k) 73.9 g, b.p. 90°C (5 mm), 97%.

After 223 g (1.10 moles) of 1,3-dichlorotetramethyldisiloxane was dissolved in 800 ml of petroleum ether, b.p. 60-90°C, and heated to 50°C, an excess of methylamine was passed over the surface of the stirred mixture, which was maintained at 50-55°C by periodic cooling with an ice bath. After 152 g (calcd., 148 g) of methylamine hydrochloride was filtered off, the solvent was removed in a rotary evaporator, then rapidly distilled. Fractional distillation through a 30-in. spinning-band column gave 62.9 g (35%) of decamethyl-1,5-dioxa-3,7-diaza-2,4,6,8-tetrasilacyclooctane, b.p. 93°C (5 mm), g.l.c purity 93.3% (2-meter column packed with SF 96 on 100/120 mesh Gas Chrom Q, 150°C, He carrier, flow rate 34 ml/min).

Redistillation of 76.2 g of various impure fractions of the subject compound through a 30-in. spinning-band column gave 63.5 g (86% recovery) of decamethyl-1,5-dioxa-3,7-diaza-2,4,6,8-tetrasilacyclooctane, b.p. 88°C (5 mm), g.l.c. purity 95.3% (same conditions).

In a repetition of the preparation with 0.69 mole of 1,3-dichlorotetramethyldisiloxane, the yield was 52% and the product distilled at 88-89°C (5 mm), g.l.c. purity 96.6% (2-meter column packed with SF 96 on 100/120 mesh Gas Chrom Q, 124°C, He carrier, flow rate 37 ml/min) [reported, b.p. 87-88°C (5 mm)] (Ref. 6).

3. Heptamethyl-1,3-dioxa-5-aza-2,4,6-trisilacyclohexane: In a procedure similar to the one described for decamethyl-1,5-dioxa-3,7-diaza-2,4,6,8-tetrasilacyclooctane, 298 g (1.08 moles) of 1,5-dichlorohexamethyltrisiloxane and an excess of methylamine gave 145 g (calcd., 146 g) of methylamine hydrochloride and 165.2 g (65%) of hexamethyl-1,3-dioxa-5-aza-2,4,6-trisilacyclohexane, b.p. 83-85°C (51 mm), after it was distilled

through a 12-in. vacuum-jacketed column packed with Berl saddles. The g.l.c. purity of a 93-g portion of this distillate was near 100% (2-meter column packed with 100/120 mesh SF 96 on Gas Chrom Q, 102°C, He carrier, flow rate 40 ml/min).

In a 0.96-molar preparation, 73% of heptamethyl-1,3-dioxa-5-aza-2,4,6-trisilacyclohexane, b.p. 87°C (55 mm), n_D^{20} 1.4100, was obtained [reported b.p. 60-61°C (17 mm), n_D^{20} 1.4100] (Ref. 6).

4. Nonamethyl-1,3,5-trioxa-7-aza-2,4,6,8-tetrasilacyclooctane: Methylamine was introduced over the surface of a solution of 178 g (0.575 mole) of 1,7-dichlorooctamethyltetrasiloxane dissolved in 1 liter of petroleum ether, b.p. 60-90°C, which had been previously heated to 50°C, until excess methylamine condensed in the exit trap. Occasional cooling with an ice bath was required during the addition to maintain the temperature of the mixture at 50°C. After the mixture was cooled, 79.1 g (calcd., 77.6 g) of methylamine hydrochloride was filtered off. Fractional distillation on a 30-in. spinning-band column gave 109 g (61%) of nonamethyl-1,3,5-trioxa-7-aza-2,4,6,8-tetrasilacyclooctane, b.p. 77°C (7 mm), n_D^{20} 1.4218 [reported b.p. 84-85°C (8 mm), n_D^{20} 1.4202] (Ref. 6), g.l.c. purity, 97.5% (2-meter column packed with SF 65 on 100/120 mesh Gas Chrom Q, 150°C, He carrier, flow rate 36 ml/min).

5. 1,3-Bis(3,3,3-trifluoropropyl)-1,3-dichloro-1,3-dimethyldisiloxane and 1,3,5-trimethyl-1,3,5-tris(3,3,3-trifluoropropyl)trisiloxane: To a solution of 28.8 g (0.14 mole) of dichloromethyl-3,3,3-trifluoropropylsilane in 20 ml of toluene, which was heated at 85°C, was added a solution of 1.22 g (0.068 mole) of water dissolved in 1.61 g of pyridine over a 0.5-hr period. After the mixture was heated for an additional hour, cooled, filtered, and the toluene distilled off, a preliminary distillation gave 14.2 g of distillate boiling 63-105°C (0.6 mm) and 8.1 g of recovered dichloromethyl-3,3,3-trifluoropropylsilane. Redistillation gave 7.0 g (28%) of 1,3-bis(3,3,3-trifluoropropyl)-1,3-dichloro-1,3-dimethyldisiloxane, b.p. 61-63°C; infrared spectrum, Figure 6; n.m.r. peaks (CCl_4) at τ 9.45 (6H singlet, $SiCH_3$) τ 8.76-9.05 (4H multiplet, $SiCH_2$), and τ 7.57-8.03 (4H multiplet, CH_2CF_3) and 4.7 g (24%) of 1,5-dichloro-1,3,5-trimethyl-1,3,5-tris(3,3,3-trifluoropropyl)trisiloxane, b.p. 95°C (0.6 mm); infrared spectrum, Figure 7; n.m.r. peaks (CCl_4) at τ 9.77 (3H singlet, $OSi(CH_3)O$), τ 9.49 (6H singlet, $ClSi(CH_3)O$), τ 8.79-9.09 (6H multiplet, $SiCH_2$), and τ 7.59-8.22 (6H multiplet, CH_2CF_3).

Anal. Calcd. for $C_8H_{14}Cl_2F_6OSi_2$: C, 26.16; H, 3.84; F, 31.04; Si, 15.30. Found: C, 26.43; H, 3.80; F, 31.45; Si, 15.80.

Anal. Calcd. for $C_{12}H_{21}Cl_2F_9O_2Si_3$: C, 27.53; H, 4.04; F, 32.67; Si, 16.10. Found: C, 27.15; H, 3.99; F, 32.02; Si, 15.21.

In a second experiment with 100 g. (0.47 mole) of dichloromethyl-3,3,3-trifluoropropylsilane and 4.32 g (0.24 mole) of water in 5.59 g of pyridine, 16.1 g of recovered dichloromethyl-3,3,3-trifluoropropylsilane, 24.6 g (28%) of 1,3-bis(3,3,3-trifluoropropyl)-1,3-dichloro-1,3-dimethyldisiloxane, b.p. 63-65°C (1.6 mm) and 22.3 (32%) of 1,5-dichloro-1,3,5-trimethyl-1,3,5-tris(3,3,3-trifluoropropyl)trisiloxane, b.p. 109-111°C (1.6 mm) were obtained.

C. Synthesis of Cyclodisilazane Monomers and Intermediates

1. N,N'-Bis(chloroethylmethylsilyl)-2,4-diethyl-2,4-dimethylcyclodisilazane: A solution of 9.5 ml (0.015 mole) of 1.6 M n-butyllithium in hexane was added dropwise to a solution of 3.4 g (0.015 mole) of 1,3-dichloro-1,3-diethyl-1,3-dimethyldisilazane in 20 ml of petroleum ether, b.p. 60-90°C, which was cooled to -65°C in an isopropyl alcohol-Dry Ice bath. After the mixture was slowly warmed to room temperature and the solvent removed by distillation at 70°C, the residue was heated at 175°C for 1 hr, cooled, taken up in 40 ml of petroleum ether, and filtered to remove 0.7 g (calcd. 0.6 g) of lithium chloride. Vacuum distillation of the filtrate gave 1.2 g (41%) of N,N'-bis(chloroethylmethylsilyl)-2,4-diethyl-2,4-dimethylcyclodisilazane, b.p. 114°C (0.20 mm); infrared spectrum, Figure 8 [reported b.p., 118-120°C (0.3 mm)] (Ref. 7a).

2. 2,4,6-Trimethyl-2,4,6-triphenylcyclotrisilazane: A solution of 81 g (4.8 moles) of ammonia in 800 ml of petroleum ether, b.p. 60-90°C, which was cooled in an isopropyl alcohol-Dry Ice bath, was treated with 191 g (1.0 mole) of dichloromethylphenylsilane over a period of 0.75 hr, and the mixture was warmed to room temperature. Filtration afforded 104.1 g (calcd 107 g) of ammonium chloride. After the filtrate was concentrated in a rotary evaporator at 50°C, vacuum distillation of the residue through a short-path column gave 121 g (91%) of 2,4,6-trimethyl-2,4,6-triphenylcyclotrisilazane, b.p. 208-212°C (0.5 mm) [reported b.p. 195-197°C (0.05 mm)] (Ref. 1d).

3. 1,3-Dichloro-1,3-dimethyl-1,3-diphenyldisilazane: After 20.3 g (0.050 mole) of mixed isomers of 2,4,6-trimethyl-2,4,6-triphenylcyclotrisilazane and 47.8 g (0.250 mole) of dichloromethylphenylsilane were heated at 150°C for 1.5 hr, distillation gave the following fractions: (a) 46.3 g, b.p. 32°C (0.4 mm) to 100 (0.1 mm), mostly recovered dichloromethylphenylsilane, (b) 33.9 g, b.p. 128-140°C (0.1 mm), mostly 1,3-dichloro-1,3-dimethyl-1,3-diphenyldisilazane, and (c) 10.8 g of residue (69% yield). Redistillation of fraction (b) gave 22.5 g of purer material, b.p. 134°C

(0.1 mm); infrared spectrum, Figure 9; n.m.r. peaks (CCl_4) at τ 9.36 and τ 9.46 (6H two singlets, $SiCH_3$) and τ 2.17-2.71 (10H multiplet, SiC_6H_5), [reported b.p. 158-160°C (0.2 mm)] (Ref. 1e). The infrared and n.m.r. spectra of the 3.6-g residue indicated that it had predominately a cyclodisilazane structure.

4. N,N'-Bis(chloromethylphenylsilyl)-2,4-dimethyl-2,4-diphenylcyclodisilazane: After 37.5 ml (0.059 mole) of 1.6 M n-butyllithium in hexane was added over a period of 0.75 hr to a solution of 1,3-dichloro-1,3-dimethyl-1,3-diphenyldisilazane, which was maintained at -65°C during the addition, the mixture was slowly warmed to room temperature and subsequently heated until the solvent had distilled from the mixture. The residue was heated at 285°C for 1 hr., cooled, dissolved in 50 ml of toluene, and 2.5 g (calcd. 2.1 g) of lithium chloride was filtered off. After the filtrate was concentrated in a rotary evaporator, fractional distillation gave 12.4 g (72%) of N,N'-bis(chloromethylphenylsilyl)-2,4-dimethyl-2,4-diphenylcyclodisilazane, b.p. 220-221°C (0.2 mm), m.p. 70-110°C; infrared spectrum, Figure 10 [reported b.p. 218-220°C (0.2 mm)] (Ref. 7b).

5. 2,4,6-Trimethyl-2,4,6-tris(3,3,3-trifluoropropyl)cyclotrisilazane: An excess of freshly distilled ammonia was added to a solution of 31.6 g (0.15 mole) of dichloromethyl(3,3,3-trifluoropropyl)silane in 300 ml of petroleum ether, b.p. 60-90°C, while the mixture was maintained at a temperature of 50°C. After the mixture had been heated at 50°C for 1 hr, it was cooled and 17.3 g (calcd. 16.0 g) of ammonium chloride was filtered off. When the filtrate was concentrated on a rotary evaporator at 25°C, vacuum distillation of the 22.3-g residue gave 18.2 g (79%) of 2,4,6-trimethyl-2,4,6-tris(3,3,3-trifluoropropyl)cyclotrisilazane, b.p. 100-110°C (0.20 mm); infrared spectrum, Figure 11 [reported b.p. 134-136°C (1.0 mm)] (Ref. 1d).

A repetition of the procedure with 55.8 g (0.27 mole) of dichloromethyl-3,3,3-trifluoropropylsilane in 500 ml of petroleum ether, b.p. 60-90°C, at 50°C gave 31.1 g (calcd. 28.4 g) of ammonium chloride and 29.2 g (72%) of 2,4,6-trimethyl-2,4,6-tris(3,3,3-trifluoropropyl)cyclotrisilazane boiling in the range of 102-112°C (0.1 mm). The purity of the compound was verified by its infrared spectrum.

Another replication of the experiment with 44.1 g (0.21 mole) of dichloromethyl-3,3,3-trifluoropropylsilane gave 23.7 g (73%) of 2,4,6-trimethyl-2,4,6-tris(3,3,3-trifluoropropyl)cyclotrisilazane, boiling in the range of 100-108°C (0.08 mm), which was characterized by its infrared spectrum. A final repetition of the procedure with 54.0 g (0.256 mole) of dichloromethyl-3,3,3-trifluoropropylsilane gave 28.7 g (73%) of the subject compound, which was collected in the boiling range of 100-108°C (0.2 mm).

6. 1,3-Bis(3,3,3-trifluoropropyl)-1,3-dichloro-1,3-dimethyldisilazane:

a. By the condensation of dichloromethyl(3,3,3-trifluoropropyl)-silane with ammonia (attempted): To 31.6 g (0.15 mole) of dichloromethyl-(3,3,3-trifluoropropyl)silane dissolved in 300 ml of petroleum ether, b.p. 60-90°C, and cooled to 10°C, was added 3.9 g (0.23 mole) of freshly distilled ammonia. After the mixture was stirred rapidly for 0.5 hr while the temperature was maintained in the range of 10-13°C, warmed to room temperature,and filtered, 6.8 g (calcd. 8.0 g) of ammonium chloride was collected. The filtrate, concentrated on a rotary evaporator at 23°C (17.7-g residue) and vacuum distilled, gave the following fractions: (a) 5.5 g of unchanged dichloromethyl(3,3,3-trifluoropropyl)silane, b.p. 40-41°C (20 mm); (b) 2.0 g (7%) of 1,3-bis(3,3,3-trifluoropropyl)-1,3-dichloro-1,3-dimethyldisilazane, b.p. 100-102°C (0.4 mm), which was identified by its infrared spectrum; and (c) 5.6 g of impure 2,4,6-trimethyl-2,4,6-tris-(3,3,3-trifluoropropyl)cyclotrisilazane, b.p. 108-117°C (0.4 mm), also identified by its infrared spectrum.

b. By the equilibration of 2,4,6-trimethyl-2,4,6-tris(3,3,3-trifluoropropyl)cyclotrisilazane and dichloromethyl(3,3,3-trifluoropropyl)-silane (1:5 mole ratio): When 14.4 g (0.031 mole) of 2,4,6-trimethyl-2,4,6-tris(3,3,3-trifluoropropyl)cyclotrisilazane and 32.7 g (0.155 mole) of dichloromethyl(3,3,3-trifluoropropyl)silane were heated at 145°C for 2 hr and then vacuum distilled, the following fractions were isolated: (a) 14.2 g of unchanged dichloromethyl(3,3,3-trifluoropropyl)silane, b.p. 28°C (3.5 mm) and (b) 27.0 g (79%) of 1,3-bis(3,3,3-trifluoropropyl)-1,3-dichloro-1,3-dimethyldisilazane, b.p. 72-74°C (0.3 mm); infrared spectrum, Figure 12; n.m.r. peaks (CCl_4) at τ 9.46 (6H singlet, $SiCH_3$); τ 8.77-9.07 (4H multiplet, $SiCH_2$), and τ 7.44-8.23 (4H multiplet, CH_2CF_3), g.l.c. purity, 100% (2-meter column packed with 5% SF 96 on 100/120 mesh Gas Chrom Q, 192°C, He carrier, flow rate 32 ml/min).

Anal. Calcd. for $C_8H_{15}Cl_2F_6NSi_2$: C, 26.23; H, 4.13; Cl, 19.36; F, 31.12; N, 3.82; Si, 15.34. Found: C, 26.35; H, 3.92; Cl, 19.48; F, 31.24; N, 4.15; Si, 15.65.

A repetition of the procedure with 29.1 g (0.062 mole) of 2,4,6-trimethyl-2,4,6-tris(3,3,3-trifluoropropyl)cyclotrisilazane and 66.0 g (0.31 mole) of dichloromethyl-3,3,3-trifluoropropylsilane gave 55.0 g (80%) of 1,3-bis(3,3,3-trifluoropropyl)-1,3-dichloro-1,3-dimethyldisilazane boiling in the range of 78-84°C (0.4 mm) and 17.9 g of recovered dichloromethyl-3,3,3-trifluoropropylsilane.

The procedure, repeated with 29.8 g (0.064 mole) of 1,3,5-trimethyl-1,3,5-tris(3,3,3-trifluoropropyl)cyclotrisilazane and 68.5 g (0.33 mole) of dichloromethyl-3,3,3-trifluoropropylsilane, gave 28.8 g of

recovered dichloromethyl-3,3,3-trifluoropropylsilane, b.p. 50-52°C (51 mm) and 55.5 g (79%) of the subject compound, b.p. 73-75°C (0.4 mm). A final replication of the method with 23.7 g (0.051 mole) of 2,4,6-trimethyl-2,4,6-tris(3,3,3-trifluoropropyl)cyclotrisilazane and 53.6 g (0.25 mole) of dichloromethyl-3,3,3-trifluoropropylsilane gave 45.2 g (81%) of 1,3-bis(3,3,3-trifluoropropyl)-1,3-dichloro-1,3-dimethyldisilazane, b.p. 81°C (1.0 mm) and 22.8 g of recovered dichloromethyl(3,3,3-trifluoropropyl)silane, b.p. 48-49°C (43 mm).

7. N,N'-Bis[chloromethyl(3,3,3-trifluoropropyl)silyl]-2,4-bis-(3,3,3-trifluoropropyl)-2,4-dimethylcyclodisilazane: A solution of 6 ml (0.01 mole) of 1.6 M n-butyllithium in hexane was added dropwise to a suspension of 3.7 g (0.01 mole) of 1,3-bis(3,3,3-trifluoropropyl)-1,3-dichloro-1,3-dimethyldisilazane in 20 ml of petroleum ether, b.p. 60-90°C, which was cooled to -65°C in an isopropyl alcohol-Dry Ice bath. After the mixture was slowly warmed to room temperature and the solvent removed by distillation at 70°C, the residue was heated at 300°C for 1.3 hr, cooled, taken up in 25 ml of toluene, and filtered to remove 0.9 g (calcd. 0.4 g) of lithium chloride. A short-path distillation of the filtrate gave 2.9 g of crude N,N'-bis[chloromethyl(3,3,3-trifluoropropyl)silyl]-2,4-bis(3,3,3-trifluoropropyl)-2,4-dimethylcyclodisilazane.

In a second experiment, 36 ml (0.056 mole) of 1.6 M n-butyllithium in hexane and 20.5 g (0.056 mole) of 1,3-bis(3,3,3-trifluoropropyl)-1,3-dichloro-1,3-dimethyldisilazane in 100 ml of petroleum ether, the intermediate lithium salt being heated at 270-300°C for 1.5 hr, gave the following fractions: (a) 11.4 g (67%) of N,N'-bis[chloromethyl(3,3,3-trifluoropropyl)silyl]-2,4-bis(3,3,3-trifluoropropyl)-2,4-dimethylcyclodisilazane, b.p. 130-132°C (0.20 mm); infrared spectrum, Figure 13 [reported b.p. 131-139°C (0.04 mm)] (Ref. 7c); (b) 2.5 g (14%) of a fraction which was mostly N,N'-bis[chloromethyl(3,3,3-trifluoropropyl)silyl]-2,4-bis(3,3,3-trifluoropropyl)-2,4-dimethylcyclodisilazane, b.p. 140-165°C (0.2 mm); and (c) 2.2 g of a high residue not distilling at 168°C (0.20 mm).

Another replication of the experiment with 55.0 g (0.15 mole) of 1,3-bis(3,3,3-trifluoropropyl)-1,3-dichloro-1,3-dimethyldisilazane in 200 ml of petroleum ether, b.p. 60-90°C, and 94 ml (0.15 mole) of 1.6 M n-butyllithium in hexane, in which the lithium salt was heated at 270-300°C for 1.5 hr, gave 35.0 g (71%) of N,N'-bis(chloromethyl-3,3,3-trifluoropropyl)-2,4-bis(3,3,3-trifluoropropyl)-2,4-dimethylcyclodisilazane, boiling in the range of 134-142°C (0.1 mm). The substance was characterized by its infrared spectrum. The compound was 88% pure by g.l.c. (2-meter column, 5% SF 96 on Gas Chrom Q, 204°C flow rate 32 ml/min, He carrier).

A preparation with 45.2 g (0.12 mole) of 1,3-bis(3,3,3-trifluoropropyl)-1,3-dichloro-1,3-dimethyldisilazane in 150 ml of petroleum ether and 77 ml (0.12 mole) of 1.6 M n-butyllithium in hexane, in which the intermediate salt was heated at 240-270°C for 1.5 hr, was purified in three consecutive fractional distillations. In each distillation the following fractions were obtained: First distillation - (a) b.p. 105°C, 2.8 g; (b) b.p. 110-120°C (0.04 mm), 1.5 g; (c) b.p. 132-136°C (0.2 mm), 7.9 g; (d) b.p. 138°C (0.2 mm), 18.2 g; (e) b.p. 139°C (0.2 mm), 3.0 g (the infrared spectra indicated that fractions (c), (d), and (e) were chiefly N,N'-bis(chloromethyl-3,3,3-trifluoropropylsilyl)-2,4-bis(3,3,3-trifluoropropyl)-2,4-dimethylcyclodisilazane, yield 71%; second distillation [fractions (c), (d), and (e)] - (f) b.p. 112-121°C (0.03 mm), 1.1 g; (g) b.p. 122-127°C (0.03 mm), 2.3 g; (h) b.p. 128-129°C (0.04 mm), 22.5 g; third distillation [fraction (h)] - (i) b.p. 112-122°C (0.03 mm), 4.1 g; (j) b.p. 124-126°C (0.03 mm), 16.3 g. The g.l.c. analyses of all fractions showed multiple peaks, with only minor enrichment of the major component. The g.l.c. trace for fraction (j) is shown in Figure 14.

Another preparation with 55.5 g (0.15 mole) of 1,3-bis(3,3,3-trifluoropropyl)-1,3-dichloro-1,3-dimethyldisilazane in 200 ml of petroleum ether and 94 ml (0.15 mole) of 1.6 M n-butyllithium in hexane, in which the intermediate lithium salt was heated at 270-290°C for 1.5 hr, gave upon distillation 37.1 g (75%) of the subject compound, b.p. 126-128°C (0.1 mm). Another experiment with 22.7 g (0.034 mole) of the chlorine-substituted cyclodisilazane derivative gave, after the product was distilled twice, 12.6 g (55%) of the subject compound, b.p. 124-126°C (0.08 mm).

8. N,N'-Bis[(dimethylamino)methyl-3,3,3-trifluoropropylsilyl]-2,4-bis(3,3,3-trifluoropropyl)-2,4-dimethylcyclodisilazane: To a solution of 8.9 g (0.196 mole) of dimethylamine in 220 ml of toluene was added a solution of 32.4 g (0.049 mole) of N,N'-bis(chloromethyl-3,3,3-trifluoropropyl)-2,4-bis(3,3,3-trifluoropropyl)-2,4-dimethylcyclodisilazane in 125 ml of toluene while the temperature of the mixture was maintained at -60°C. The mixture, warmed to room temperature and stored over the weekend, gave 8.5 g (calcd. 8.0 g) of dimethylamine hydrochloride when it was filtered. Evaporation of the solvent gave a crystalline residue, which after a preliminary distillation, provided 27.6 g of distillate boiling in the range of 126-152°C (0.1 mm). Redistillation of a 25.5-g portion of this distillate gave the following fractions: (a) 1.9 g, b.p. 120-124°C (0.1 mm); (b) 5.7 g, b.p. 128-132°C (0.1 mm); (c) 14.7 g, b.p. 132-134°C (0.1 mm); and (d) 2.7 g, b.p. 134-135°C (0.1 mm) [reported b.p. 138-147°C (0.2 mm)] (Ref. 7d). The total distillate represented a 76% yield, but the infrared spectra of all the fractions contained an Si_2NH absorption in the 900-950 cm^{-1} region. The fractions were combined and washed with petroleum ether, b.p. 60-90°C, to produce 5.0 g of a solid, m.p. 101-106°C. G.l.c. analysis of the solid portion (Figure 15) and the 17.1-g liquid portion

recovered from solvent showed main peak purities of 83%, and 54%, respectively. A number of other components present in significant quantities were present in the g.l.c. traces. Redistillation of the soluble portion did not improve the purity. The infrared spectrum of the product prior to being washed with petroleum ether exhibited a weak absorption in the 900-950 cm^{-1} region, but the absorption was absent in the washed sample (Figure 16).

Anal. (the 101-106°C melting sample) Calcd. for $C_{20}H_{40}F_{12}N_4Si_4$: C, 35.49; H, 5.95; F, 33.68; N, 8.28; Si, 16.60. Found: C, 35.61; H, 6.01; F, 33.89; N, 8.15; Si, 16.68.

Samples of impure N,N'-bis[(dimethylamino)methyl-3,3,3-trifluoropropylsilyl]2,4-bis(3,3,3-trifluoropropyl)-2,4-dimethylcyclodisilazane totalling 28.6 g were combined and redistilled in an annular spinning-band column. The following fractions were collected: (a) 2.9 g, b.p. 111-120°C (0.05 mm); (b) 1.0 g, b.p. 120-121°C (0.05 mm); (c) 3.9 g, b.p. 122-123°C (0.05 mm); (d) 13.3 g, b.p. 122-123°C (0.04 mm); and 1.4 g of a forerun. All fractions showed multiple peaks on g.l.c. analysis, the purest, fraction (d), containing about 63% of the chief component.

In a repetition of the procedure with 8.0 g (0.012 mole) of N,N'-bis-(chloromethyl-3,3,3-trifluoropropyl)-2,4-bis(3,3,3-trifluoropropyl)-2,4-dimethylcyclodisilazane, which exhibited no absorption bands in the 900-950 cm^{-1} of its infrared spectrum, 1.13 g (0.025 mole) of dimethylamine, and 15.7 ml (0.025 mole) of 1.6 M n-butyllithium in hexane gave 1.4 g (calcd. 1.06 g) of lithium chloride and 5.8 g (73%) of N,N'-bis(dimethylamino)methyl-3,3,3-trifluoropropyl-2,4-bis(3,3,3-trifluoropropyl)-2,4-dimethylcyclodisilazane, b.p. 138-140°C (0.2 mm). Its infrared absorption spectrum exhibited a weak band in the 900-950 cm^{-1} region (Figure 17).

When 37.1 g (0.057 mole) of N,N'-bis[chloromethyl(3,3,3-trifluoropropyl)silyl]-2,4-bis(3,3,3-trifluoropropyl)-2,4-dimethylcyclodisilazane was treated with dimethylamine, 28.6 g (74%) of the subject compound was obtained in a preliminary distillation. Redistillation gave 20 g (53%) of the compound, b.p. 123-125°C (0.05 mm). The band at 900-950 cm^{-1} was much weaker in the product obtained in this preparation (infrared spectra, Figure 18).

D. Synthesis of Miscellaneous Monomers and Intermediates

1. 1,1,1-Trichloro-3,3,3-trimethyldisilazane: After 242 g (1.5 moles) of hexamethyldisilazane was added to 1,020 g (6.0 moles) of silicon tetrachloride while the mixture was maintained at 25°C, the mixture was stirred for 14 hr and stored for 2 days. The volatile chlorosilanes were removed under vacuum while the mixture was maintained at room temperature.

Vacuum distillation of the residue gave 269 g (81%) of 1,1,1-trichloro-3,3,3-trimethyldisilazane, b.p. 73-77°C (35 mm), n.m.r. peak (CCl_4) at τ 9.76 (singlet, $SiCH_3$). Upon storage, the distillate became cloudy. Redistillation gave 248 g of 1,1.1-trichloro-3,3,3-trimethyldisilazane, b.p. 74-75°C (35 mm), which showed a single peak on g.l.c. analysis (2-meter column, 5% SF 96 on Gas Chrom Q, 124°C, flow rate 32 ml/min, He carrier) [reported b.p. 70-72°C (35 mm)] (Ref. 8). This sample also became cloudy after storage.

Anal. Calcd. for $C_3H_{10}Cl_3NSi_2$: C, 16.18; H, 4.53; Cl, 47.77; N, 6.29; Si, 25.23. Found: C, 16.04; H, 4.42; Cl, 47.75; N, 6.41; Si, 25.32.

A g.l.c. analysis made 23 days after the final distillation showed an impurity peak constituting approximately 2.3% of the total composition.

2. Methyltris(ethylamino)silane: After 65 g (0.50 mole) of trichloromethylsilane was added to a solution of 135 g (213 ml, 3.00 moles) of ethylamine dissolved in 1.5 liters of petroleum ether, b.p. 35-60°C, while the solution was maintained at 10°C, the mixture was warmed to room temperature and stored overnight. The ethylamine hydrochloride was filtered off, the filtrate was concentrated on a rotary evaporator, and the residue was vacuum distilled. There was obtained 65.9 g (75%) of methyltris(ethylamino)silane, b.p. 64°C (10 mm), n_D^{20} 1.4302; infrared spectrum, Figure 19; n.m.r. peaks (CCl_4) at τ 10.11 (3H singlet, $SiCH_3$), τ 8.98 (9H triplet J = 7 cps, $NHCH_2\underline{CH_3}$), and τ 7.23 (6H pentuplet J = 7 cps, $NHCH_2CH_3$). [Reported b.p. 62-63°C (10 mm), n_D^{20} 1.4300] (Ref. 9).

3. 1,1-Dichloro-1,3,3,3-tetramethyldisilazane (attempted): To 180 g (1.20 moles) of trichloromethylsilane, which was stirred rapidly, was added 48.3 g (0.30 mole) of hexamethyldisilazane, and stirring was continued for 10 hr. After the volatile silicon halides were removed under reduced pressure, the residue was fractionally distilled. A total of 26.7 g (55%) of hexamethyldisilazane was recovered in the boiling range of 42-58°C (36 mm) and identified by its n.m.r. spectrum. A 15.2-g fraction, b.p. 58-70°C (36 mm), was thought to contain 1,1-dichloro-1,3,3,3-tetramethyldisilazane [n.m.r. peaks (CCl_4) at τ 9.82, τ 9.59, and τ 9.24 with area ratios of about 3:5:1]. Upon redistillation of the fraction at 32 mm, only 7.9 g of material was recovered. A 2.1-g fraction, b.p. 72°C (32 mm); infrared spectrum, Figure 20, was possibly 1,1-dichloro-1,3,3,3-tetramethyldisilazane, and 4.5 g. of a solid residue. The liquid quickly became cloudy on storage.

4. 2,5-Bis(ethylamino)2,5-dimethyl-1,3,4,6-tetraethylspiro[3.3]-trisilazane: A solution of 26.3 g (0.15 mole) of methyltris(ethylamino)silane in 50 ml of petroleum ether, b.p. 60-90°C, was maintained at 25°C while 188 ml (0.30 mole) of 1.6 M n-butyllithium in hexane was added. Stirring

was continued for 1.5 hr, then 12.8 g (0.075 mole) of silicon tetrachloride was added again with the temperature maintained at 25°C. After the mixture was refluxed overnight, filtration gave 13.1 g (calcd. 12.7 g) of lithium chloride. Subsequent evaporation of the solvent and vacuum distillation gave 9.0 g (32%) of 2,5-bis(ethylamino)-1,2,3,4,5,6-hexamethylspiro[3.3]-trisilazane, b.p. 134-138°C (0.1 mm), n_D^{20} 1.4598, infrared spectrum, Figure 21, n.m.r. peaks (CCl_4) at τ 9.97 (6H singlet, $SiCH_3$), τ 9.03 (18H triplet, J = 7 cps, CH_2CH_3), τ 7.14 (12H total, quadruplet, J = 7 cps, NCH_2CH_3 and pentuplet, J = 7 cps, $NHCH_2CH_3$).

Anal. Calcd. for $C_{14}H_{38}N_6Si_3$: C, 44.87; H, 10.22; N, 22.43; Si, 22.48. Found: C, 44.38; H, 9.95; N, 22.78; Si, 22.98.

5. Bis[2-(1,3-diethyl-4-ethylamino-2,4-dimethyl)cyclodisilazanyl]-ethylamine: A mixture of 35 g (0.20 mole) of methyltris(ethylamino)silane and 0.2 g (0.002 mole) of ammonium bromide was heated to 340°C over a period of 80 hr. The chief fractions that were obtained on vacuum distillation were (a) 10.8 g (49%), b.p. 130-131°C (0.1 mm), and (b) 8.5 g (38%), b.p. 136-138°C (0.1 mm); infrared spectrum, Figure 22. Fraction (b), which solidified on storage, had n.m.r. peaks (CCl_4) at τ 10.00 (6H singlet, $SiCH_3$), τ 9.82 (6H singlet, $SiCH_3$), τ 8.98 (21H triplet J = 7 cps CH_2CH_3), and τ 7.16 (14H multiplet, CH_2CH_3). Fraction (b) was tentatively identified as bis[2-(1,3-diethyl-4-ethylamino-2,4-dimethyl)cyclodisilazanyl]ethylamine. Pearce identified the same product as N-pentaethylbis(ethylamino)tetramethylbiscyclotetrasilazane, b.p. 140-147°C (0.6 mm), m.p. 84°C (Ref. 10).

For correlation of the spectral data with similar structures, Fink found an asymmetric stretch frequency of 955 cm^{-1} for Si_2NH in 1,3-diethyl-2,2,4,4-tetramethylcyclodisilazane (Ref. 11). Lienhard reported the H^1 chemical shift as τ 9.89 for $SiCH_3$ in hexamethylcyclodisilazane (Ref. 12). In studies of the thermolysis of methyltrianilinosilane, Fink asserts a preference for the biscyclodisilazanyl structure.

E. Polymerization of Arylenedisilanols and Cyclosiloxazanes

1. Preliminary polymerizations: The polymers in Table VI were prepared by heating mixtures of the specified monomers in the absence of solvent under the indicated conditions in a Wood's metal bath. After the polymerization was completed, the residues were devolatilized under vacuum for several hours. Solubilities were determined by mixing the polymers with 500 ml of toluene (or a portion of the polymer with an equivalent amount of toluene) for several days, filtering off the insoluble portion, and removing the absorbed solvent under vacuum.

TABLE VI

PRELIMINARY POLYMERIZATIONS

Experiment No.	Decamethyl-1,5-dioxa-3,7-diaza-2,4,6,8-tetrasila-cyclooctane (moles)	Hexamethyl-1,3-dioxa-5-aza-2,4,6-trisilacyclohexane (moles)	p-Phenylenebis-(dimethylsilanol) (moles)	Oxydi-p-phenylene-bis(dimethylsilanol) (moles)	p-Phenylenebis-(methylvinyl-silanol)	Heating Conditions	Insoluble Portion (wt %)	Inherent Viscosity of Soluble Portion (dl/g)
1	0.0110	--	--	0.0200 (Batch B)	--	160°C for 4 hr	84	--
2	0.0035	--	--	0.0067 (Batch B)	--	120°C for 1 hr 120-160°C in 1 hr 160°C for 4 hr	24	--
3	0.0035	--	--	0.0067 (Batch B)	--	120°C for 4 hr	None	Low mol. wt. soft polymer
4	0.0035	--	0.0067	--	--	160°C for 4 hr	None	0.70
5	0.0035	--	0.0067	--	--	125°C for 2 hr 125-160°C for 1 hr	None	0.81
6	0.0035	--	0.0067	--	--	160°C for 4 hr (flask rotated)	None	0.67
7	--	0.0105	--	0.0100 (Batch B)	--	160°C for 4 hr	43	--
8	--	0.0105	0.0100	--	--	160°C for 4 hr	None	0.64
9	0.0035	--	--	0.0067 (Batch A)	--	160°C for 4 hr	None	2.05
10	0.00500	--	0.00950	--	0.00050	160°C for 4 hr	0.2	0.67
11	0.00500	--	0.00950	--	0.00050	160°C for 4 hr	2.2	0.49
12	0.0050	--	0.0100	--	--	160°C for 4 hr	None	0.70

In another experiment, a mixture of 1.1294 g (5% excess, 0.0035 mole) of 100% g.l.c. pure decamethyl-1,5-dioxa-3,7-diaza-2,4,6,8-tetrasilacyclooctane and 2.1340 g (0.0067 mole) of bis(p-hydroxydimethylsilylphenyl) ether in 20 ml of toluene was stirred at room temperature for 0.5 hr and then heated over steam for 2 hr under nitrogen. The solvent was removed on a rotary evaporator at 50°C and the residual mixture was heated at 160°C for 8 hr in a Wood's metal bath under nitrogen. An occasional vacuum was employed during the heating period to remove any residual solvent. After the polymer, η_{inh} = 0.20 dl/g, was heated at 60°C for 3 hr under a vacuum of 1 mm to remove the last trace of toluene, its inherent viscosity was 0.24 dl/g.

In a parallel experiment the same quantity of each monomer was weighed directly into the reaction flask and heated at 160°C for 4 hr in a Wood's metal bath under nitrogen. The polymer contained 0.271 g (9%) of toluene-insoluble material, but the soluble portion of the polymer had an inherent viscosity of 0.51 dl/g.

2. Preparation of polymers without the use of inhibitors: Polymer syntheses are summarized in Tables VII-XII. Specified quantities of monomers were heated in a Wood's metal bath at the indicated temperatures and times. After the polymers were stirred with an excess of toluene for 18 hr, the solutions were filtered and the insoluble portion was dried and weighed. The toluene solutions were then stirred with portions of water, which were separated periodically until the extracts were neutral. After the polymer solutions were dried over sodium sulfate, the solvent was removed on a rotary evaporator and the residue was stored under vacuum at 50°C until solvent odor was no longer evident. When the polymers were not washed with water, they were stored under vacuum for 2 hr before their properties were determined.

In some 10-g batches, the internal temperature of the polymer was monitored in 4-hr polymerizations at 160°C and the following readings were obtained: After 1 hr, 142°C; 2 hr, 132°C; 3 hr, 130°C; 4 hr, 130°C.

3. Preparation of Polymers with the use of inhibitors: In a preliminary series of experiments, the monomers specified in Table XIII were heated at 160°C for 4 hr, cooled, and the polymers were stirred with 300 ml of toluene overnight to determine their solubility.

The polymers in Tables XIV-XVIII were prepared by heating mixtures of the specified quantities of monomers in a Wood's metal bath. After the polymer was cooled, it was mixed with toluene (about 1 liter/10 g of polymer) overnight and the insoluble portion, if any, was filtered off, dried, and weighed. The solution was stirred with 100-ml portions of water and the water phases were separated until the extracts were neutral. After the solvent was evaporated at 50°C in a rotary evaporator, the inherent viscosity and yield were determined.

TABLE VII

POLYMERIZATION OF DECAMETHYL-1,5-DIOXA-3,7-DIAZA-2,4,6,8-TETRASILACYCLOOCTANE WITH OXYDI-p-PHENYLENEBIS(DIMETHYLSILANOL)

Experiment No.	Notebook/ Date	Decamethyl-1,5-dioxa-3,7-diaza-2,4,6,8-tetrasilacyclooctane (sample/g/mole)	Oxydi-p-phenylenebis(dimethylsilanol) (sample/g/mole)	Conditions (T °C/hr)	Insolubles	Inherent Viscosity (dl/g)	Note
1	71-54-47 6/2/71	71-11-100-5 3.807 0.0118 (5% excess)	71-54-35 7.134 0.00224	160 4	none	1.99	a
2	71-54-58 6/9/71	71-11-100-5 1.1294 0.00350 (5% excess)	71-54-35 2.1340 0.00670	160 4	none	1.55	-
3	71-54-80 6/18/71	71-11-100-5 3.808 0.0118 (5% excess)	71-54-35 7.134 0.0224	160 4	none	2.45	b,c
4	71-54-82 6/18/71	71-11-100-5 3.614 0.0112 (no excess)	71-54-35 7.134 0.0224	160 4	none	0.89	d,c
5	71-54-84 6/18/71	71-11-100-5 3.614 0.0112 (no excess)	71-54-35 7.134 0.0224	160 4	none	0.86	e
6	71-54-86 6/18/71	71-11-100-5 3.808 0.0118 (5% excess)	71-54-35 7.134 0.0224	160 1	none	0.80	f
7	71-54-88 6/19/71	71-11-100-5 1.1294 0.00350 (no excess)	71-54-46 2.2296 0.00700	160 4	none	0.48	-
8	71-54-24 5/17/71	71-11-100-5 1.1294 0.00350 (5% excess)	71-54-4 2.1340 0.00670	160 4	not completely soluble	-	-
9	71-54-26 5/17/71	71-11-100-5 1.1294 0.00350 (5% excess)	71-54-5 2.1340 0.00670	160 4	not completely soluble	-	-
10	71-54-28 5/18/71	71-11-100-5 1.1294 0.00350 (5% excess)	1169-174A 2.1340 0.00670	160 4	none	0.95	-
11	71-54-30 5/18/71	71-11-100-5 1.1294 0.00350 (5% excess)	1169-174 2.1340 0.00670	160 4	not completely soluble	-	-
12	71-54-41 5/27/71	71-11-100-5 1.1294 0.00350 (5% excess)	71-54-35 2.1340 0.00670	160 4	none	1.24	-

a. 89% yield; b. 96% yield; c. Not water washed; d. 98% yield; e. 94% yield; f. 97% yield.

TABLE VIII

POLYMERIZATION OF DECAMETHYL-1,5-DIOXA-3,7-DIAZA-2,4,6,8-TETRASILACYCLOOCTANE OR HEPTAMETHYL-1,3-DIOXA-5-AZA-2,4,6-TRISILACYCLOHEXANE WITH p-PHENYLENEBIS(DIMETHYLSILANOL)

Experiment No.	Notebook/ Date	Decamethyl-1,5-dioxa-3,7-diaza-2,4,6,8-tetrasila-cyclooctane (sample/g/mole)	Heptamethyl-1,3-dioxa-5-aza-2,4,6-trisilacyclohexane (sample/g/mole)	p-Phenylenebis-(dimethylsilanol) (sample/g/mole)	Conditions (T °C/hr)	Insolubles	Inherent Viscosity (dl/g)
1	71-54-18 5/13/71	71-11-100-3 1.1294 0.00350 (5% excess)	-	918-117 1.5169 0.00670	160 4	none	0.56
2	71-54-20 5/13/71	71-11-100-4 1.1294 0.00350 (5% excess)	-	918-117 1.5619 0.00670	160 4	none	0.77
3	71-54-22 5/14/71	71-11-100-5 1.1294 0.00350 (5% excess)	-	918-117 1.5169 0.00670	160 4	none	0.43
4	71-54-32 5/19/71	-	71-54-11-3 1.2365 0.005250 (5% excess)	918-117 1.1321 0.00500	160 4	none	0.57

TABLE IX

POLYMERIZATION OF DECAMETHYL-1,5-DIOXA-3,7-DIAZA-2,4,6,8-TETRASILACYCLOOCTANE, p-PHENYLENEBIS-(DIMETHYLSILANOL), AND p-PHENYLENEBIS(METHYLVINYLSILANOL)

Experiment No.	Notebook/ Date	Decamethyl-1,5-dioxa-3,7-diaza-2,4,6,8-tetrasilacyclooctane (sample/g/mole)	p-Phenylenebis(dimethylsilanol) (sample/g/mole)	p-Phenylenebis(methylvinylsilanol) (sample/g/mole)	Conditions (T °C/hr)	Insolubles (g/%)	Inherent Viscosity (dl/g)	Note
1	71-11-21 2/25/71	70-142-37-8 1.6135 0.00500 (no excess)	918-117 2.1509 0.00950	69-116-62A 0.1252 0.00050 (5 mole %)	160 4	0.008 0.2	0.67	a
2	71-11-25 3/1/71	70-142-37-8 1.6135 0.00500 (no excess)	918-117 2.1509 0.00950	69-116-62A 0.1252 0.000500 (5 mole %)	160 4	0.078 2.2	0.49	a
3	71-54-66 6/14/71	70-142-37-8 1.6135 0.00500 (no excess)	918-117 2.1509 0.00950	69-116-62A 0.1252 0.000500 (5 mole %)	160 4	1.47 41	-	-

a/ Not water washed.

TABLE X

POLYMERIZATION OF DECAMETHYL-1,5-DIOXA-3,7-DIAZA-2,4,6,8-TETRASILACYCLOOCTANE, OXYDI-p-PHENYLENEBIS-(DIMETHYLSILANOL), AND OXYDI-p-PHENYLENEBIS(METHYLVINYLSILANOL)

Experiment No.	Notebook/ Date	Decamethyl-1,5-dioxa-3,7-diaza-2,4,6,8-tetrasilacyclooctane (sample/g/mole)	Oxydi-p-phenylenebis(dimethylsilanol) (sample/g/mole)	Oxydi-p-phenylenebis(methylvinylsilanol) (sample/g/mole)	Conditions (T °C/hr)	Insolubles (g/%)	Inherent Viscosity (dl/g)
1	70-137-17 10/16/70	777-55 7.196 0.0223 (no excess)	1169-147A 13.473 0.0423	69-116-95-2 0.771 0.00225 (5 mole %)	160 4	0.4 1.9	0.41
2	70-137-19 10/19/70	777-55 7.228 0.0224 (no excess)	169-147A 13.983 0.0439	69-116-95-2 0.308 0.00090 (2 mole %)	160 4	0.6 2.8	0.72
3	71-54-70 6/15/71	71-11-100-5 1.033 0.00320 (no excess)	71-54-35 1.998 0.00627	69-116-95-2 0.044 0.00013 (2 mole %)	160 4	1.1 34	-

TABLE XI

POLYMERIZATION OF DECAMETHYL-1,5-DIOXA-3,7-DIAZA-2,4,6,8-TETRASILACYCLOOCTANE, OXYDI-p-PHENYLENEBIS-(DIMETHYLSILANOL), AND p-PHENYLENEBIS(METHYLVINYLSILANOL)

Experiment No.	Notebook/ Date	Decamethyl-1,5-dioxa-3,7-diaza-2,4,6,8 tetrasilacyclooctane (sample/g/mole)	Oxydi-p-phenylene bis(dimethyl-silanol) (sample/g/mole)	p-Phenylenebis-(methylvinyl-silanol) (sample/g/mole)	Conditions (T °C/hr)	Insolubles (g/%)	Inherent Viscosity (dl/g)	Note
1	70-137-57 11/17/70	838-22 7.228 0.0224 (no excess)	1169-147B 13.983 0.0439	69-116-62A 0.225 0.00090 (2 mole %)	160 4	0.19 0.9	0.40	-
2	70-137-59 11/17/70	838-22 7.196 0.0223 (no excess)	1169-147B 13.473 0.0423	69-116-62A 0.563 0.00225 (5 mole %)	160 4	1.07 5	0.54	-
3	71-54-38 5/25/71	71-11-100-5 3.807 0.0118 (5% excess)	1169-147A 6.784 0.0213	69-116-62A 0.250 0.00112 (5 mole %)	160 4	5.0 46	-	-
4	71-54-43 5/28/71	71-11-100-5 3.807 0.0118 (5% excess)	71-54-35 6.784 0.213	69-116-62A 0.250 0.00112 (5 mole %)	160 4	6.6 61	-	-
5	71-54-49 6/3/71	71-11-100-5 1.1352 0.00352 (5% excess)	71-54-35 2.2073 0.00637	69-116-62A 0.0839 0.000335 (5 mole %)	160 0.5	0.23 7.7	-	-
6	71-54-51 6/4/71	71-11-100-5 1.1352 0.00352 (5% excess)	71-54-35 2.0273 0.00637	69-116-62A 0.0839 0.000335 (5 mole %)	140 0.5	none	0.21	-
7	71-54-53 6/7/71	71-11-100-5 1.1352 0.00352 (5% excess)	71-54-35 2.0273 0.00637	69-116-62A 0.0839 0.000335 (5 mole %)	140 1.5	not completely soluble	-	-
8	71-54-60 6/10/71	71-11-100-5 3.614 0.0112 (no excess)	71-54-35 6.991 0.0220	69-116-62A 0.113 0.000450 (2 mole %)	160 4	7.6 76	-	-
9	71-54-62 6/11/71	71-11-100-5 1.205 0.00373 (no excess)	1169-147B 2.330 0.00732	69-116-62A 0.038 0.000152 (2 mole %)	160 4	1.4 41	-	-
10	71-54-64 6/11/71	70-142-37-8 1.205 0.00373 (no excess)	71-54-35 2.330 0.00732	69-116-62A 0.038 0.000152 (2 mole %)	160 4	1.3 38	-	-
11	71-54-68 6/14/71	71-11-100-5 1.270 0.00394 (5% excess)	71-54-35 2.261 0.00710	69-116-62A 0.083 0.000331 (5 mole %)	heated gradually with mantle and mixing	3.0 85	-	-
12	71-54-72 6/15/71	71-11-100-5 1.1352 0.00350 (5% excess)	71-54-35 2.1232 0.00667	69-116-62A 0.0084 0.0000335 (0.5 mole %)	160 4	none	2.48	-

TABLE XI (Concluded)

Experiment No.	Notebook/ Date	Decamethyl-1,5-dioxa-3,7-diaza-2,4,6,8 tetrasilacyclooctane (sample/g/mole)	Oxydi-p-phenylene bis(dimethyl-silanol) (sample/g/mole)	p-Phenylenebis-(methylvinyl-silanol) (sample/g/mole)	Conditions (T °C/hr)	Insolubles (g/%)	Inherent Viscosity (dl/g)	Note
13	71-54-75 6/16/71	71-11-100-5 1.1352 0.00350 (5% excess)	71-54-35 2.1232 0.00667	69-116-62A 0.0084 0.0000335 (0.5 mole %)	160 4	1.9 60	-	-
14	71-54-78 6/16/71	71-11-100-5 1.1352 0.003517 (5% excess)	71-54-35 2.1124 0.00663	69-116-62A 0.0168 0.0000670 (1 mole %)	160 4	2.8 91	-	-
15	71-54-88 6/19/71	71-11-100-5 1.1294 0.00350 (no excess)	71-54-35 2.2273 0.00699	69-116-62A 0.0018 0.000007 (0.1 mole %)	160 4	none	-	-
16	71-54-88 6/19/71	71-11-100-5 1.1294 0.003500 (no excess)	71-54-35 2.2250 0.006986	69-116-62A 0.0036 0.0000140 (0.2 mole %)	160 4	none	-	-
17		71-11-100-5 1.1294 0.003500 (no excess)	71-54-35 2.2204 0.006972	69-116-62A 0.0072 0.0000280 (0.4 mole %)	160 4	none	-	-
18	71-54-93 6/21/71	71-11-100-5 1.1294 0.00350 (no excess)	71-54-35 2.2273 0.006993	69-116-62A 0.0018 0.000007 (0.1 mole %)	140 4	none	-	-
19		71-11-100-5 1.1294 0.003500 (no excess)	71-54-35 2.2250 0.006986	69-116-62A 0.0036 0.000014 (0.2 mole %)	140 4	none	-	-
20		71-11-100-5 1.1294 0.003500 (no excess)	71-54-35 2.2204 0.006972	69-116-62A 0.0072 0.000028 (0.4 mole %)	140 4	none	-	-
21		71-11-100-5 1.1294 0.003500 (no excess)	71-54-35 2.2073 0.006930	69-116-62A 0.01753 0.000070 (1.0 mole %)	140 4	trace	-	-
22	71-76-1 6/23/71	71-11-100-5 3.808 0.0118 (5% excess)	71-54-35 6.8480 0.02150	69-116-62A 0.2244 0.000896 (4 mole %)	140 4	8.0 81	-	-
23	71-76-3 6/24/71	71-11-100-5 3.795 0.01176 (5% excess)	71-54-35 7.1059 0.02231	69-116-62A 0.02244 0.0000896 (0.4 mole %)	140 4	none	0.71	-
24	71-54-99 6/21/71	71-11-100-5 1.1859 0.003675 (5% excess)	71-54-46 2.2296 0.007000	69-116-62A 0.0701 0.00028 (4 mole %)	160 4	none	0.41	a
25	71-54-100 6/21/71	71-11-100-5 1.1859 0.003675 (5% excess)	71-54-46 2.2296 0.007000	69-116-62A 0.0351 0.00014 (2 mole %)	160 4	none	1.15	a

a. Vinyl monomer was added to toluene solution of polymer after polymerization and the mixture was refluxed 2 hr prior to being water washed.

TABLE XII

POLYMERIZATION OF HEPTAMETHYL-1,3-DIOXA-5-AZA-2,4,6-TRISILACYCLOHEXANE, OXYDI-p-PHENYLENEBIS-(DIMETHYLSILANOL), AND p-PHENYLENEBIS(METHYLVINYLSILANOL)

Experiment No.	Notebook/ Date	Heptamethyl-1,3-dioxa-5-aza-2,4,6-tetrasilacyclohexane (sample/g/mole)	Oxydi-p-phenylenebis(dimethylsilanol) (sample/g/mole)	p-Phenylenebis-(methylvinylsilanol) (sample/g/mole)	Conditions (T °C/hr)	Insolubles (g/%)	Inherent Viscosity (dl/g)	Note
1	71-76-29 7/1/71	71-54-11-3 1.7590 0.00747 (no excess)	71-54-46 2.3300 0.00732	69-116-62A 0.03800 0.000152 (2 mole %)	160 4	none	0.30	a
2	71-76-33 7/2/71	71-54-11-3 1.7590 0.00747 (no excess)	71-54-46 2.3310 0.00732	69-116-62A 0.0370 0.000149 (2 mole %)	160 4	none	-	-
3	71-76-35 7/2/71	71-54-11-3 1.7590 0.00747 (no excess)	71-54-46 2.2595 0.00709	69-116-62A 0.0940 0.000373 (5 mole %)	160 4	none	-	-
4	71-76-41 7/12/71	71-54-11-3 4.7406 0.02013 (5% excess)	71-54-46 5.9848 0.01879	69-116-62A 0.0901 0.0003834 (2 mole %)	160 4	1.3 13	-	-
5	71-76-43 7/12/71	71-54-11-3 4.7406 0.02013 (5% excess)	71-54-46 5.8000 0.01821	69-116-62A 0.2400 0.000959 (5 mole %)	160 4	5.6 56	-	-
6	71-76-45 7/13/71	71-54-11-3 4.5149 0.0192 (no excess)	71-54-46 5.9848 0.0188	69-116-62A 0.09601 0.000383 (2 mole %)	160 4	none	0.52	b
7	71-76-47	71-54-11-3 4.5149 0.0192 (no excess)	71-54-46 5.800 0.0182	69-116-62A 0.2400 0.000959 (5 mole %)	160 4	none	0.46	c
8	71-76-55 7/19/71	71-54-11-3 4.5149 0.01917 (no excess)	71-54-46 6.0453 0.01898	69-116-69A 0.04800 0.0001917 (1 mole %)	160 4	none	0.36	d
9	71-76-58 7/19/71	71-54-11-3 4.5149 0.01917 (no excess)	71-54-46 5.9848 0.01879	69-116-62A 0.09601 0.0003834 (2 mole %)	160 4	none	0.46	b
10	71-76-65 7/21/71	71-54-11-3 4.5600 0.01936 (1% excess)	71-54-46 6.0453 0.01898	69-116-62A 0.0480 0.0001917 (1 mole %)	160 4	none	0.47	b
11	71-76-68 7/21/71	71-54-11-3 4.6052 0.01955 (2% excess)	71-54-46 6.0453	69-116-62A 0.0480 (1 mole %)	160 4	1.6 16	-	-

a. 100% yield; b. 90% yield; c. 82% yield; d. 99% yield.

TABLE XIII

PRELIMINARY INHIBITOR INVESTIGATION

Experimental No.	Notebook/ Date	Decamethyl-1,5-dioxa 3,7-diaza-2,4,6,8-tetrasilacyclooctane (sample/g/mole)	Oxydi-p-phenylene-bis(dimethylsilanol) (sample/g/mole)	p-Phenylenebis-(methylvinyl-silanol) (sample/g/mole)	Inhibitor (Compound/ Wt. %)	Insolubles (g/%)	Inherent Viscosity (dl/g)
1	71-106-1 8/30/71	71-142-37-8 1.11294 0.0035 (5% excess)	71-76-84 2.1340 (0.006700)	--	--	None	--
2	71-106-3 8/31/71	71-142-37-8 1.2714 0.003940 (5% excess)	71-54-46 2.2614 (0.00710)	69-116-62A 0.0829 0.000331 (4.5 mole %)	phenothia-zine, 0.1	Trace	1.37
3	71-106-5 8/31/71	71-142-37-8 1.2714 0.003940 (5% excess)	71-54-46 2.2614 0.00710	69-116-62A 0.0829 0.000331 (4.5 mole %)	phenyl-α-naphthyl-amine, 0.1	0.23 6.7	--
4	71-106-7 8/31/71	71-142-37-8 1.2714 0.00394 (5% excess)	71-54-46 2.2614 0.00710	69-116-62A 0.0829 0.000331 (4.5 mole %)	--	1.10 32	--
5	71-106-9 9/2/71	71-142-37-8 1.2714 0.00394 (5% excess)	71-54-46 2.2614 0.00710	69-116-69A 0.0829 0.000331 (4.5 Mole %)	phenothia-zine, 0.1	Trace	0.89
6	71-106-11 9/2/71	71-142-37-8 1.2714 0.00394 (5% excess)	71-54-46 2.2614 0.00710	69-116-62A 0.0829 0.000331 (4.5 mole %)	phenothia-zine, 0.05	0.077 2.2	1.93

TABLE XIV

POLYMERIZATION OF DECAMETHYL-1,5-DIOXA-3,7-DIAZA-2,4,6,8-TETRASILACYCLOOCTANE WITH OXYDI-p-PHENYLENEBIS(DIMETHYLSILANOL) OR p-PHENYLENEBIS(DIMETHYLSILANOL) IN THE PRESENCE OF PHENOTHIAZINE

Experiment No.	Notebook/ Date	Decamethyl-1,5-dioxa-3,7-diaza-2,4,6,8-tetrasilacyclooctane 71-76-90-5 2.5175 g 0.007802 Mole (5% Excess)	Decamethyl-1,5-dioxa-3,7-diaza-2,4,6,8-tetrasilacyclooctane 71-76-90-5 2.4456 g 0.007579 Mole (2% Excess)	Oxydi-p-phenylenebis-(dimethylsilanol) 71-54-46 4.5228 g 0.01420 Mole	Oxydi-p-phenylenebis-(dimethylsilanol) 71-54-46 4.6407 g 0.01457 Mole	p-Phenylenebisdimethylsilanol 69-116-62A 0.0744 g 0.0002970 Mole (2 mole %)	p-Phenylenebisdimethylsilanol 69-116-62A 0.1658 g 0.000662 Mole (4.5 Mole %)	Insolubles (g/%)	Inherent Viscosity (dl/g)	Yield (%)
1	71-106-13 9/3/71	x		x			x	0.75 11	2.07	90
2	71-106-15 9/3/71	x		x			x	None	1.55	91
3	71-106-17 9/3/71		x	x			x	3.5 52	--	--
4	71-106-19 9/7/71		x	x			x	None	0.36	90
5	71-106-21 9/7/71		x	x[a/]			x	None	0.35	98
6	71-106-23 9/7/71	x			x	x		Trace	1.05	83
7	71-106-25 9/7/71	x			x	x		Trace	1.13	96
8	71-106-27 9/8/71		x		x	x[a/]		None	0.38	94
9	71-106-29 9/8/71		x		x	x[a/]		None	0.38	97

a/ Sample 71-76-84.

TABLE XV

POLYMERIZATION OF DECAMETHYL-1,5-DIOXA-3,7-DIAZA-2,4,6,8-TETRASILACYCLOOCTANE, HEPTAMETHYL-1,3-DIOXA-5-AZA-2,4,6-TRISILACYCLOHEXANE, OR NONAMETHYL-1,3,5-TRIOXA-7-AZA-2,4,6,8 TETRASILACYCLOOCTANE WITH OXYDI-p-PHENYLENEBIS(DIMETHYLSILANOL) AND p-PHENYLENE-BIS(METHYLVINYLSILANOL) IN THE PRESENCE OF PHENOTHIAZINE

Experiment No.	Notebook/ Date	Cyclosiloxazane (sample/g/mole)	Oxydi-p-phenylene-bis(dimethylsilanol) (sample/g/mole)	p-Phenylenebis-(methylvinylsilanol) (sample/g/mole)	Phenothia-zine (g/%)	Insolubles (g/%)	Inherent Viscosity (dl/g)	Yield (%)
1	71-106-51 9/22/71	Decamethyl-1,5-dioxa-3,7-diaza-2,4,6,8-tetrasilacyclooctane 71-76-90-5 3.8387 g 0.01186 mole (5% excess)	71-76-84 6.8798 0.02160	69-116-62A 0.2554 0.00102 (4.5 mole %)	0.0101 0.1	7.75 77	--	--
2	71-106-59 9/24/71	Decamethyl-1,5-dioxa-3,7-diaza-2,4,6,8-tetrasilacyclooctane 71-106-57 3.8287 g 0.01186 mole (5% excess)	71-76-84 6.8798 0.02160	69-116-62A 0.2554 0.00102 (4.5 mole %)	0.0202 0.2	None	1.45	93
3	71-106-53 9/22/71	Heptamethyl-1,3-dioxa-5-aza-2,4,6-trisila-cyclooctane 71-54-11-3 4.7406 g 0.02013 mole (5% excess)	71-76-84 5.8332 0.01831	69-116-62A 0.2161 0.000863 (4.5 mole %)	0.0100 0.1	None	0.94	89
4	71-106-55 9/22/71	Nonamethyl-1,3,5-trioxa-7-aza-2,4,6-trisilacyclooctane 71-106-44 5.5273 g 0.01785 mole (5% excess)	71-76-84 5.5273 0.01785	69-116-62A 5.1726 0.01624 (4.5 mole %)	0.0101 0.1	0.25 2.5	2.60	93

TABLE XVI

POLYMERIZATION OF DECAMETHYL-1,5-DIOXA-3,7-DIAZA-2,4,6,8-TETRASILACYCLOOCTANE OR NONAMETHYL-1,3,5-TRIOXA-7-AZA-2,4,6,8-TETRASILACYCLOOCTANE WITH OXYDI-p-PHENYLENEBIS(DIMETHYLSILANOL) OR p-PHENYLENEBIS(DIMETHYLSILANOL) AND p-PHENYLENEBIS(METHYLVINYLSILANOL) IN THE PRESENCE OF PHENOTHIAZINE

Experiment No.	Notebook/ Date	Decamethyl-1,5-dioxa-3,7-diaza-2,4,6,8-tetrasilacyclooctane (sample/g/mole)	Nonamethyl-1,3,5-trioxa-7-aza-2,4,6,8-tetrasilacyclooctane (sample/g/mole)	Oxydi-p-phenylenebis-(dimethylsilanol) (sample/g/mole)	p-Phenylenebis-(dimethylsilanol) (sample/g/mole)	p-Phenylenebis-(methylvinylsilanol)	Phenothiazine (g/%)	Insolubles (g/%)	Inherent Viscosity (dl/g)
1	71-106-79 10/6/71		71-106-74 8.1673 0.02638 (5% excess)	combined 7.6411 0.02399		69-116-62A 0.2830 0.001130 (4.5 mole %)	0.0149 0.1	9.2 62	--
2	71-106-81 10/8/71		71-106-44 6.4311 0.02077 (5% excess)	combined 6.1727 0.01938		69-116-62A 0.0991 0.000396 (2 mole %)	0.0121 0.1	0.55 4.5	3.71
3	71-106-87 10/14/71	71-106-57 6.7765 0.02100 (5% excess)			918-117 8.8757 0.3920	69-116-62A 0.2003 0.000800 (2 mole %)	0.0143 0.1	None	0.45
4	71-106-89 10/15/71	71-106-57 5.3670 0.01663 (5% excess)		71-125-11 9.8866 0.03104		69-116-62A 0.1586 0.0006334 (2 mole %)	0.0142 0.1	None	1.78
5	71-106-91 10/15/71	71-106-57 5.3670 0.01663 (5% excess)		71-125-11 9.8866 0.03104		69-116-62A 0.1586 0.0006334 (2 mole %)	0.0142 0.1	None	1.82
6	71-106-75 10/5/71	71-106-57 0.6292 0.001950 (5% excess)		1169-147A 1.1301 0.003548		69-116-62A 0.0418 0.000167 (4.5 mole %)	0.0017 0.1	None	--
7	71-106-77 10/5/71	71-106-57 0.6292 0.001950 (5% excess)		71-76-28-3 1.1301 0.003548		69-116-62A 0.0418 0.000167 (4.5 mole %)	0.0017 0.1	0.838 51	--
8	71-105-85 10/14/71	71-106-57 0.6292 0.001950 (5% excess)		71-125-11 1.1597 0.003641		69-116-62A 0.0186 0.0000743 (2 mole %)	0.0017 0.1	None	--

TABLE XVII

POLYMERIZATION OF DECAMETHYL-1,5-DIOXA-3,7-DIAZA-2,4,6,8-TETRASILACYCLOOCTANE, OXYDI-p-PHENYLENEBIS(DIMETHYLSILANOL), AND p-PHENYLENEBIS(DIMETHYLSILANOL) IN THE PRESENCE OF PHENOTHIAZINE

Experiment No.	Notebook/Date	Decamethyl-1,5-dioxa-3,7-diaza-2,4,6,8-tetrasilacyclooctane (sample/g/mole)	Oxydi-p-phenylenebis(dimethylsilanol) (sample/g/mole)	p-Phenylenebis(methylvinylsilanol) (sample/g/mole)	Phenothiazine (g/%)	Polymerization Conditions (°C/hr)	Inherent Viscosity (dl/g)	Yield (%)
1	71-139-19 11/1/71	71-106-57 5.3670 0.01663 (5% excess)	71-125-11 9.8866 0.03104	69-116-62A 0.1586 0.0006334 (2 mole %)	0.0142 0.1	160 4	1.42	97
2	71-139-21 11/1/71	71-106-57 5.3670 0.01663 (5% excess)	71-125-11 9.8866 0.03104	69-116-69A 0.1586 0.0006334 (2 mole %)	0.0142 0.1	160 4	1.78	98
3	71-139-23 11/2/71	71-106-57 0.6292 0.001950 (5% excess)	71-125-11 1.1358 0.003566	69-116-69A 0.0373 0.000149 (4 mole %)	0.0017 0.1	140 4	0.31	76
4	71-139-25 11/2/71	71-106-57 0.6292 0.001950 (5% excess)	71-125-11 1.1358 0.003566	69-116-69A 0.0373 0.000149 (4 mole %)	0.0017 0.1	140 3	0.41	82
5	71-139-33 11/5/71	71-106-57 5.3670 0.01663 (5% excess)	71-125-11 9.6827 0.03040	69-116-69A 0.3173 0.001267 (4 mole %)	0.0142 0.1	140 4	0.57	99
6	71-139-35 11/5/71	71-106-56 5.3670 0.01663 (5% excess)	71-125-11 9.6827 0.03040	69-116-69A 0.3173 0.001267	0.0142 0.1	140 4	0.48	100

TABLE XVIII

POLYMERIZATION OF DECAMETHYL-1,5-DIOXA-3,7-DIAZA-2,4,6,8-TETRASILACYCLOOCTANE, HEPTAMETHYL-1,3-DIOXA-5-AZA-2,4,6-TRISILACYCLOOCTANE, OR NONAMETHYL-1,3,5-TRIOXA-7-AZA-2,4,6,8-TETRASILACYCLOOCTANE WITH OXYDI-p-PHENYLENEBIS(DIMETHYLSILANOL) OR p-PHENYLENEBIS(DIMETHYLSILANOL) AND p-PHENYLENEBIS(METHYLVINYLSILANOL) IN THE PRESENCE OF PHENOTHIAZINE

Experiment No.	Notebook/ Date	Decamethyl-1,5-dioxa-3,7-diaza-2,4,6,8-tetrasilacyclooctane (sample/g/mole)	Nonamethyl-1,3,5-trioxa-7-aza-2,4,6-tetrasilacyclooctane	Heptamethyl-1,3-dioxa-5-aza-2,4,6-trisilacyclohexane	Oxydi-p-phenylenebis(dimethylsilanol) (sample/g/mole)	p-Phenylenebis(dimethylsilanol) (sample/g/mole)	p-Phenylenebis(methylvinylsilanol) (sample/g/mole)	Phenothiazine (g/%)	Polymerization Conditions (°C/hr)	Inherent Viscosity (dl/g)	Yield (%)
1	71-139-65 11/24/71	71-106-57 3.7948 0.01176 (5% excess)			71-125-11 7.1346 0.02240				160 4	1.24	97
2	71-139-65 11/29/71		71-106-44 7.1919 0.02323 (5% excess)		71-125-11 6.7588 0.02122		69-116-62A 0.2214 0.000884 (4 mole %)	0.0131 0.1	160 4	2.69	94
3	71-139-69 11/29/71			69-116-62A 5.5889 0.02372 (5 mole %)	71-125-11 6.9117 0.02170		69-116-62A 0.2264 0.000904 (4 mole %)	0.0118 0.1	160 4	2.86	93
4	71-139-71 11/30/71	71-106-57 0.6292 0.00195 (5% excess)			71-125-11 1.0887 0.003418		69-116-62A 0.0744 0.0002972 (8 mole %)	0.0016 0.1	140 4	--	--
5	71-139-75 12/2/71	71-125-31 5.0350 0.01560 (5% excess)			71-125-11 8.7081 0.027		69-116-62A 0.5955 0.002378 (8 mole %)	0.0132 0.1	140 4	1.82	88
6	71-139-99 12/17/71	71-125-31 6.2683 0.01943 (5% excess)			71-125-11 11.3135 0.03552		69-116-62A 0.3706 0.001480 (4 mole %)	0.0165 0.1	140 4	1.03	84
7	71-158-1 12/17/71	71-125-31 9.4871 (0.02940) (5% excess)				918-117 12.1723 0.05376	69-116-62A 0.5610 0.002240 (4 mole %)	0.0200 0.1	140 4	0.54	98

The monomer mixtures described in Tables XIV-XVI were heated at 160°C for 4 hr; those in Tables XVII or XVIII for the specified times at the specified temperatures. Each batch described in Table XV contained 0.1% (0.0072 g) of phenothiazine. The inhibitor and its quantity are specified in the other tables. No insoluble polymer resulted in the polymerizations reported in Tables XVII and XVIII.

F. Compounding, Curing, and Testing of Arylenedisilanol-Cyclosiloxazane Elastomers

1. Preliminary cure studies: After the experimental polymers were milled with Hi Sil 233 and tert-butyl peroxybenzoate (100 parts of polymer to 40 parts of filler to 1.7 parts of catalyst), the compounded materials were heated in a mold at 300°F for 30 min. The results are summarized in Table XIX.

2. Preliminary determination of physical test data: In this series each experimental polymer was milled in the proportion of 100 parts of polymer, 40 parts of Hi Sil 233, and the indicated number of parts of tert-butyl peroxybenzoate. After the compounded materials were cured at 300°F for 30 min, the samples were postcured in an air circulating oven as follows: The temperature of the oven was increased in 50°F increments from 100-400°F over an 8-hr period then maintained at 400°F for 12 hr. Samples cut for testing were about 20 mils thick and were cut with a dog-bone die, one-half the size of die C, ASTM D-412-66. Tensile strengths and elongation at break were determined in accordance with the same specification. The results are reported in Table XX.

3. Evaluation of experimental polymers: Results of physical tests in the evaluation of experimental polymers are summarized in Tables XXI-XXVIII. The polymers were all milled with Hi Sil 233 and tert-butyl peroxybenzoate and optionally with Mapico Red, each component used at the specified level. The samples were press cured at 300°F unless otherwise specified and post cured at 400°F for 20 hr in a forced air oven after being heated to 400°F in 50°F increments over a 7-hr period. Ultimate tensile strengths, percent elongations, and 50% modulus were determined on an Instron Tensile Tester.

The elastomers in Tables XXII and XXIII were all prepared with 40 parts of Hi Sil 233 and no Mapico Red.

The series described in Table XXIV, in which low filler levels were examined, included an additional polymer (Table XVI-2, $\eta = 3.71$). This polymer sample could not be milled satisfactorily, and the filler was not homogeneously dispersed, even at the 5, 10, and 15 parts levels.

TABLE XIX

PRELIMINARY POLYMER CURE STUDIES

Experiment No.	Polymer (table reference)	Polymer Preparation	Polymer Inherent Viscosity (dl/g)	Results
1	XI-23	0.4% vinyl, 5% excess siloxazane,[a] polymerized for 3 hr at 140°C, water washed.	0.71	No cure
2	XI-1	2% vinyl, no excess siloxazane,[a] polymerized for 4 hr at 160°C, water washed.	0.40	Cure
3	XI-2	5% vinyl, no excess siloxazane,[a] polymerized for 4 hr at 160°C, water washed.	0.54	Cure
4	VII-3	No vinyl, 5% excess siloxazane,[a] polymerized for 4 hr at 160°C, no water wash.	2.45	No cure
5	VII-4	No vinyl, no excess siloxazane,[a] polymerized for 4 hr at 160°C, no water wash.	0.89	No cure
6	VII-5	No vinyl, no excess siloxazane,[a] polymerized for 4 hr at 160°C, water washed.	0.86	No cure
7	VII-6	No vinyl, no excess siloxazane,[a] polymerized for 4 hr at 160°C, water washed.	0.80	No cure
8	XI-24	4% vinyl added after polymerization, 5% excess siloxazane,[a], polymerized for 4 hr at 160°C, water washed.	0.41	No cure
9	XI-25	2% vinyl added after polymerization, 5% excess siloxazane,[a] polymerized for 4 hr at 160°C, water washed.	1.15	No cure
10	XII-6	2% vinyl, no excess siloxazane,[b] polymerized for 4 hr at 160°C, water washed.	0.52	Cure
11	XII-6	5% vinyl, no excess siloxazane,[b] polymerized for 4 hr at 160°C, water washed.	0.46	Cure

a/ Decamethyl-1,5-dioxa-3,7-diaza-2,4,6,8-tetrasilacyclooctane.
b/ Heptamethyl-1,3-dioxa-5-aza-2,4,6-trisilacyclohexane.

TABLE XX

PRELIMINARY PHYSICAL TEST DATA FOR CURED EXPERIMENTAL POLYMERS

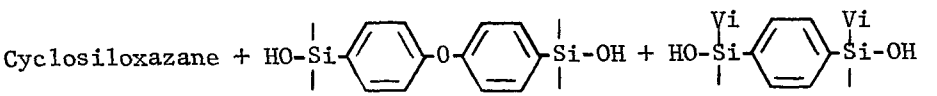
Experiment No.	Polymer (table reference)	Polymer Inherent Viscosity (dl/g)	Vinyl Content (%)	Catalyst (parts)	Elongation at Break (%)	Tensile Strength (psi)	Modulus at 50% Elongation (psi)
1	XII-10[b/]	0.47	1	0.6	125[a/]	430	250
2	XII-10[b/]	0.47	1	1.7	230	670	160
3	XII-10[b/]	0.47	1	3.0	74	280	200
4	XII-9	0.46	2	0.6	92	390	270
5	XII-9	0.46	2	1.7	131	550	280
6	XII-9	0.46	2	3.0	135	550	270
7	XII-8	0.36	1	0.6	144	430	180
8	XII-8	0.36	1	1.7	92	380	260
9	XII-8	0.36	1	3.0	175	610	200
10	XII-7	0.46	5	0.6	93	680	360
11	XII-7	0.46	5	1.7	66	710	580
12	XII-7	0.46	5	3.0	68	630	440
13	XII-6[c/]	0.52	2	1.7	122	720	310
14	XI-1	0.40	2	0.6	123	630	220
15	XI-1	0.40	2	1.7	95	670	330
16	XI-1	0.40	2	3.0	94	610	290
17	XI-2	0.54	5	0.6	78	510	310
18	XI-2	0.54	5	1.7	72	600	390
19	XI-2	0.54	5	3.0	33	150	-

a/ All values are the average of three determinations.
b/ Prepared with 1% excess cyclosiloxazane.
c/ The cured polymer was stored for 7 days at 94°C in a vented desiccator containing water.

TABLE XXI

TENSILE STRENGTH AND PERCENT ELONGATION AT BREAK OF EXPERIMENTAL ELASTOMERS: PART 1

Polymer Composition



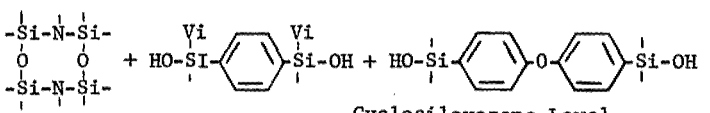
			Cyclosiloxazane						
			-Si-N-Si- O O -Si-N-Si-						
	Cyclosiloxazane Stoichiometry	Proportion of p-Phenylenebis-(methylvinylsilanol) (mole %)	Polymer (table reference/inherent viscosity, dl/g)	Catalyst Level (parts) 0.6	1.7	3.0	Polymer (table reference/inherent viscosity, dl/g)	Catalyst Level (parts) 0.6	1.7	3.0
Tensile (psi)							XII-10	430[a]	670	280
Elongation (%)	1 % Excess	1					0.47	125	230	74
50% Modulus (psi)								250	160	200
Tensile (psi)							XII-8	430	380	610
Elongation (%)	Equivalent	1					0.36	144	92	175
50% Modulus (psi)								180	260	200
Tensile (psi)			VIII-3[b]	630	670	610	XII-9	390	550	550
Elongation (%)	Equivalent	2	0.40	123	95	94	0.46	92	131	135
50% Modulus (psi)				220	330	290		270	280	270
Tensile (psi)			VIII-4[b]	510	600	150	XII-7	680	710	630
Elongation (%)	Equivalent	5	0.54	78	72	33	0.46	93	66	68
50% Modulus (psi)				310	390	-		360	580	440

a/ All values are the average of three determinations.
b/ Table VIII, Ref. 7e.

TABLE XXII

TENSILE STRENGTH AND PERCENT ELONGATION AT BREAK OF EXPERIMENTAL ELASTOMERS: PART 2

Polymer Composition



Cyclosiloxazane Level

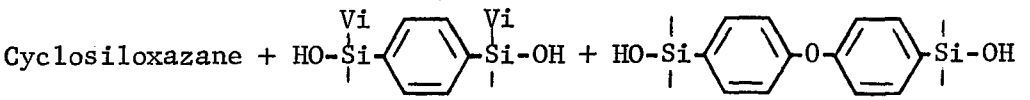
	Proportion of p-Phenylene-bis(methyl-vinylsilanol) (mole %)	2% Excess						5% Excess					
		Polymer (table Reference/ inherent viscosity, dl/g)	Catalyst Level (parts) 1.7	3.0	Polymer (table reference/ inherent viscosity, dl/g)	Catalyst Level (parts) 1.7	3.0	Polymer (table reference/ inherent viscosity, dl/g)	Catalyst Level (parts) 1.7	3.0	Polymer (table reference/ inherent viscosity, dl/g)	Catalyst Level (parts) 1.7	3.0
Tensile (psi)	2	XIV-8	561(3)[a]	341(2)	XIV-8	429(3)	320(1)	XIV-6	729(3)	636(3)	XIV-7	648(3)	392(2)
Elongation (%)		0.38	91	59	0.38	85	52	1.05	123	110	1.13	107	60
50% Modulus (psi)			330	183		255	167		542	316		333	190
Tensile (psi)	4.5	XIV-4	697(2)	775(2)	XIV-5	690(2)	748(2)	XIV-1	729(3)	313(3)	XIV-2	739(3)	549(1)
Elongation (%)		0.36	73	71	0.35	80	67	2.07	79	33	1.55	96	52
50% Modulus (psi)			312	405		394	412		356	154		356	270

a / Number of replications used in average.

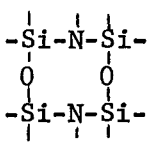
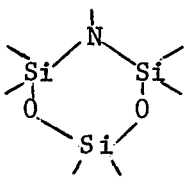
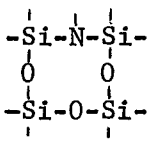
TABLE XXIII

TENSILE STRENGTH AND PERCENT ELONGATION AT BREAK OF EXPERIMENTAL ELASTOMERS: PART 3

Polymer Composition



(5% excess) (4.5 mole %)

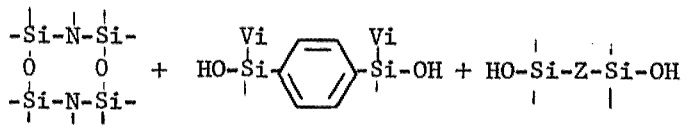
Polymer (table reference/inherent viscosity - dl/g)	Cyclosiloxazane	Catalyst (parts)	Tensile (psi)	Elongation (%)	50% Modulus (psi)
XV-2		1.7	Partial cure only		
1.45		3.0	Tears easily, bubbles		
		4.2	Bubbles		
XV-3		0.6	Partial cure, purple		
0.94		1.2	Partial cure, partly purple		
		1.7	702(2)[a]	86	319
		3.0	635(2)	77	268
XV-4		0.6	319(3)	112	198
2.60		1.2	871(2)	144	466
		1.7	558(3)	66	334

a/ Number of replications used in the average.

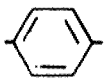
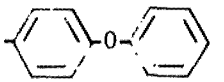
TABLE XXIV

TENSILE STRENGTH AND PERCENT ELONGATION AT BREAK OF EXPERIMENTAL ELASTOMERS: PART 4

Polymer Composition



(5% excess) (2 mole %)

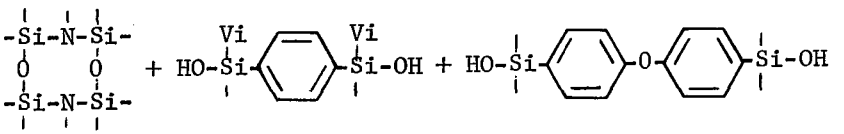
	Parts Hi Sil 233	Z =  Polymer (table reference/inherent viscosity, dl/g)	Sample Normally Cured	Z =  Polymer (table reference/inherent viscosity, dl/g)	Sample Normally Cured	Sample Heated 24 Hr at 250°C in a Bomb
Tensile (psi)		XVI-3	59.5(3)[a]	XVI-4	121(3)	Samples dark, very
Elongation (%)	5	0.45	40.0(3)	1.78	126(3)	sticky
50% Modulus (psi)			33.9(3)		73.7(3)	
Tensile (psi)		XVI-3	165(3)	XVI-4	116(3)	Samples dark, very
Elongation (%)	10	0.45	54.8(3)	1.78	109(3)	sticky
50% Modulus (psi)			78.8(3)		79.4(3)	
Tensile (psi)		XVI-3	257(3)	XVI-5	216(3)	40.3(3)
Elongation	20	0.45	58.0(3)	1.82	109(3)	156(3)
50% Modulus (psi)			113(3)		114(3)	18.7(3)
Tensile (psi)		XVI-3	573(2)	XVI-5	606(3)	126(3)
Elongation (%)	40	0.45	51.2(2)	1.82	104(3)	141(3)
50% Modulus (psi)			297(2)		324(3)	68.0(3)

a/ Number of replications used in the average.

TABLE XXV

TENSILE STRENGTH AND PERCENT ELONGATION AT BREAK OF EXPERIMENTAL ELASTOMERS: PART 5

Polymer Composition



(5% excess) (4 mole %)

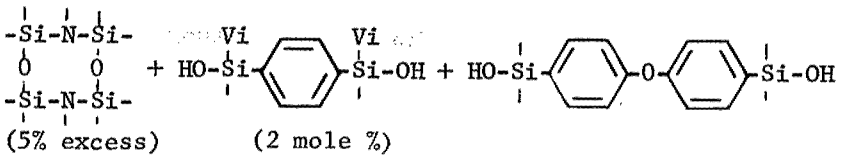
	Polymer (table reference/inherent viscosity, dl/g)	Parts Mapico Red	Cure Temperature (°F)	Parts t-Butyl peroxybenzoate	Sample Normally Cured	Sample Heated 24 Hr at 250°C in a Bomb
Tensile (psi)	XVII-5	3	280	1.7	724(3)a/	336(3)
Elongation (%)	0.57				65.5(3)	73.7(3)
50% Modulus (psi)					315(3)	129(3)
Tensile (psi)	XVII-5	3	300	1.7	675(3)	330(3)
Elongation (%)	0.57				63.7(3)	77.7(3)
50% Modulus (psi)					288(3)	124(3)
Tensile (psi)	XVII-6	3	300	1.2	728(3)	305(3)
Elongation (%)	0.48				69.3(3)	72.3(3)
50% Modulus (psi)					341(3)	131
Tensile (psi)	XVII-6	None	300	1.7	683(3)	248(2)
Elongation (%)	0.48				54.4(3)	63.0(2)
50% Modulus (psi)					298(3)	90.2(2)

a/ Number of replications used in average.

TABLE XXVI

TENSILE STRENGTH AND PERCENT ELONGATION AT BREAK OF EXPERIMENTAL ELASTOMERS: PART 6

Polymer Composition



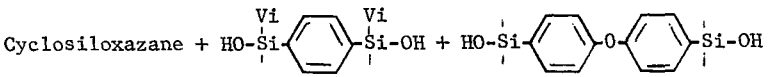
	Polymer (table reference/inherent viscosity, dl/g)	Parts Hi Sil 233	Cure Temperature (°F)	Sample Normally Cured	Sample Heated 24 Hr. at 250°C in a Bomb
Tensile (psi)	XVII-2	40	280	788(3)[a/]	142(3)
Elongation (%)	1.78			107(3)	123(3)
50% Modulus (psi)				369(3)	62.3(3)
Tensile (psi)	XVII-2	40	300	752(3)	139(3)
Elongation (%)	1.78			99.9(3)	117(3)
50% Modulus (psi)				362(3)	68.6(3)
Tensile (psi)	XVII-1	50	300	708(3)	171(3)
Elongation (%)	1.42			79.5(3)	107(3)
50% Modulus (psi)				300(3)	73.3(3)
Tensile (psi)	XVII-1	70	300	795(3)	163(2)
Elongation (%)	1.42			42.6(3)	34.9(2)
50% Modulus (psi)				341(3)	61.1(2)

a/ Number of replications used in average.

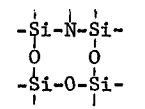
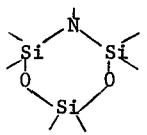
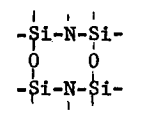
TABLE XXVII

TENSILE STRENGTH AND PERCENT ELONGATION AT BREAK OF EXPERIMENTAL ELASTOMERS: PART 7

Polymer Composition



(5% excess)

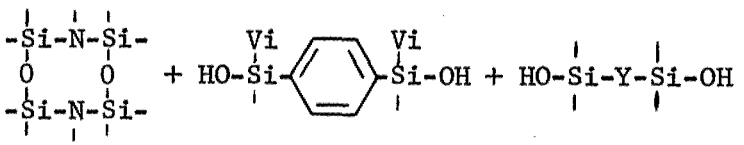
Cyclosiloxazane	Polymer (table reference/inherent viscosity, dl/g)	Mapico Red (parts)	p-Phenylenebis-(methylvinylsilanol) (mole %)	Cured Normally: Tensile (psi)	Cured Normally: Elongation (%)	Cured Normally: 50% Modulus (psi)	Sample Heated 24 hr at 250°C in a Bomb: Tensile (psi)	Sample Heated 24 hr at 250°C in a Bomb: Elongation (%)	Sample Heated 24 hr at 250°C in a Bomb: 50% (psi)
	XVIII-2 2.69	0	4	609(3)[a]	84.1(3)	392(3)	87.8(3)	117(2)	52.2(2)
		3	4	604(3)	89.7(3)	371(3)	86.2(3)	142(2)	40.8(2)
	XVIII-3 2.86	0	4	664(3)	88.2(3)	430(3)	99.1(2)	83.7(2)	60.3(2)
		3	4	654(3)	72.9(3)	401(3)	112(3)	104(3)	64.3(3)
	XVIII-5 1.82	0	8	685(2)	60.6(2)	266(3)	217(3)	72.5(3)	85.8(3)
		3	8	423(3)	40.2(3)	183(3)	234(3)	75.5(3)	84.3(3)
Commercial vinyl-substituted silicone		0	-	1,126(3)	657(3)	590(3)	Samples Lost Integrity		

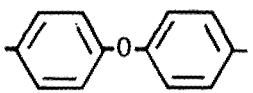
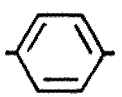
a/ Number of replications used in average.

TABLE XXVIII

TENSILE STRENGTH AND PERCENT ELONGATION AT BREAK OF EXPERIMENTAL ELASTOMERS: PART 8

Polymer Composition



Y	Polymer (table reference/inherent viscosity, dl/g)	Conditions	Tensile (psi)	Elongation (%)	50% Modulus (psi)	Weight Loss (%)
	XVIII-6	Cured normally	705(3)[a/]	174(3)	356(3)	
	1.03	After 100 hr at 500°F	532(3)	50.0(3)	214(3)	4.4
		After 300 hr at 500°F	257(3)	24.1(3)	124(3)	8.8
		After 500 hr at 500°F	407(3)	16.9(3)	219(3)	12.1
		After 500 hr in vented container with water at 65-95°C	314(3)	78.3(3)	154(3)	
	XVIII-7	Cured normally	549(3)	44.2(3)	267(3)	
	0.54	After 100 hr at 500°F	532(3)	50.0(3)	214(3)	3.6
		After 300 hr at 500°F	459(3)	24.5(3)	229(2)	6.5
		After 500 hr at 500°F	428(3)	16.7(3)	223(3)	8.5
		After 500 hr in a vented container with water at 65-95°C	349(3)	37.9(3)	173(3)	
		After 24 hr in a closed container at 250°C	393(3)	51.8(3)	176(3)	

a/ Number of replications used in average.

In this series and subsequent series, the mill rollers were heated at 160°F to aid in milling the high viscosity samples. None of the samples in Table XXIV contained Mapico Red.

All the elastomers in Tables XXV, XXVI, XXVII, and XXVIII were milled with 40 parts of Hi Sil 233 and 3 parts of Mapico Red and cured with 1.7 parts of tert-butyl peroxybenzoate, unless otherwise specified.

G. Preparation, Compound, Curing, and Testing of Polymers from Arylenedisilanols and Cyclodisilazane Derivatives

1. Synthesis and evaluation of a polymer from N,N'-bis[(diethylamino)dimethylsilyl]tetramethylcyclodisilazane, oxydi-p-phenylenebis(dimethylsilanol), and p-phenylenebis(methylvinylsilanol): After a solution of 6.0000 g (0.01482 mole) of N,N'-bis[(diethylamino)dimethylsilyl]tetramethylcyclodisilazane, 4.6248 g (0.01452 mole) of oxydi-p-phenylenebis(dimethylsilanol), and 0.0751 g (0.00030 mole) of p-phenylenebis(methylvinylsilanol) in 60 ml of toluene was stirred for 2 hr at room temperature on a steam bath. The solution was stored 7 days, the solvent removed in a rotary evaporator, and the residue heated at 100°C for 2 hr under vacuum in a Wood's metal bath. The cooled polymer dissolved in 45 ml of toluene, was treated with 15 ml of a 0.01 g/ml solution of bis(trimethylsilyl)acetamide and the mixture was heated for 2 hr on a steam bath under nitrogen. After the solvent was evaporated, the residue, heated for 2 hr under vacuum on a Wood's metal bath, had an inherent viscosity in toluene of 0.36 dl/g.

In some preliminary experiments, the aforementioned polymer and a similar polymer not containing p-phenylenebis(methylvinylsilanol) were screened to determine if they could be cured. After these polymers were milled with Hi Sil 233 and t-butyl peroxybenzoate (100 parts of polymer, 40 parts of filler, 1.7 parts of catalyst), the compounded specimens were heated in a mold at 300°F for 30 min. The results are summarized in Table XXIX. For the polymer examined in Experiment No. 2, no cure was obtained without a catalyst, and cures with 0.6 or 3.0 parts of catalyst provided specimens that were either very weak or contained bubbles.

TABLE XXIX

SCREENING OF POLYMER CONTAINING CYCLODISILAZANE GROUPS

Experiment No.	Polymer Preparation	Polymer Inherent Viscosity (dl/g)	Results
1	N,N'-Bis[(diethylamino)-dimethylsilyl]tetramethyl-cyclodisilazane-oxydi-p-phenylenebis(dimethylsil-anol) condensate	0.74	No cure
2	Same as above with 2 mole % of p-phenylenebis(methyl-vinyl)silanol	0.36	Cure

The subject polymer was then compounded in the same proportions with filler and various amounts of catalyst, cured, and post-cured in the usual way. Strength properties and percent elongation are summarized in Table XXX.

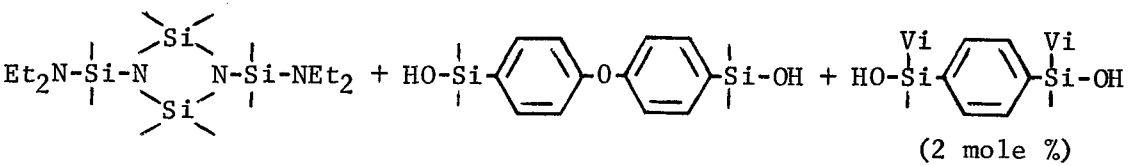
The polymer synthesis was repeated with phenothiazine added so that the molecular weight of the product could be advanced with additional heating. After a solution of 1.0123 g (0.002500 mole) of N,N'-bis[(diethylamino)dimethylsilyl]tetramethylcyclodisilazane, 0.7565 g (0.002375 mole) of oxydi-p-phenylenebis(dimethylsilanol), 0.0313 g (0.000125 mole) of p-phenylenebis(dimethylsilanol), and 0.0029 g (2 wt %) of phenothiazine in 60 ml of toluene was stirred for 2 hr at room temperature, the solvent was removed in a rotary evaporator and the residue was heated at 100°C for 2 hr under vacuum in a Wood's metal bath. The cooled polymer, dissolved in 7.5 ml toluene, was treated with 2.5 ml of a 0.01 g/ml solution of bis(trimethylsilyl)acetamide and the mixture was heated for 2 hr on a steam bath under nitrogen. After the solvent was evaporated, the residue, heated 2 hr under vacuum at 200°C, was not completely soluble in toluene.

2. Polymer from N,N'-bis[(dimethylamino)methyl-3,3,3-trifluoropropylsilyl]-2,4-bis(3,3,3-trifluoropropyl)-2,4-dimethylcyclodisilazane, oxydi-p-phenylenebis(dimethylsilanol) and p-phenylenebis(methylvinylsilanol): A mixture of 0.6769 g. (0.001000 mole) of N,N'-bis[(dimethylamino)methyl-3,3,3-trifluoropropylsilyl]-2,4-bis(3,3,3-trifluoropropyl)-2,4-dimethylcyclodisilazane, m.p. 101-106°C, 0.3021 g. (0.00095 mole) of oxydi-p-phenylenebis-(dimethylsilanol) and 0.0125 g. (0.00005 mole) of p-phenylenebis(methylvinylsilanol) was stirred for 1.1 hr at room temperature and then for

TABLE XXX

STRENGTH PROPERTIES OF A POLYMER CONTAINING CYCLODISILAZANE GROUPS

Polymer Composition



t-Butyl Peroxy-benzoate (parts)	Tensile (psi)	Elongation (%)	50% Modulus (psi)
0	No cure		
0.6	73 (3)[a/]	23	38
1.7	134 (3)	31	62
3.0	130 (3)	35	60

a/ Number of replications used in the average.

2 hr on a steam bath. After 1.0 ml of a 0.0100 g/ml solution of bis(trimethylsilyl) acetamide was added, heating was continued for an additional hour on the steam bath. Evaporation of the solvent in a rotary evaporator gave a polymer that was heated for 2 hr at 150°C in a Wood's metal bath, dissolved in 20 ml of toluene and 20 ml of petroleum ether, b.p. 60-90°C, washed with 40 ml of water, and recovered by evaporating the solvent. After the final polymer was heated at 150°C for 5 min under vacuum, its inherent viscosity was 0.08 dl/g. An additional 2-hr heating at 150°C under vacuum increased the inherent viscosity to 0.09 dl/g. A repeititon of the experiment with fivefold quantities also gave a polymer with an inherent viscosity of 0.09 dl/g. An additional preparation with threefold quantities gave a polymer with an inherent viscosity of 0.06 dl/g.

Neither polymer, milled with tert-butyl peroxybenzoate and Hi Sil 233, cured after 1 hr at 300°F.

H. Miscellaneous Properties of Experimental Polymers

1. Hydrolytic stability of polymers containing cyclodisilazane groups: Two polymers were employed in this experiment: One prepared from oxydi-p-phenylenebis(dimethylsilanol) and N,N'-bis[(dimethylamino)dimethylsilyl]-tetramethylcyclodisilazane and the other from oxydi-p-phenylenebis(dimethylsilanol) and N,N'-bis[(dimethylamino)methyl-3,3,3-trifluoropropylsilyl]-2,4-bis(3,3,3-trifluoropropyl)-2,4-dimethylcyclodisilazane. Each was cast as a film on a KRS-5 optic and both samples were stored in a desiccator containing water in an oven at 200°F. Periodically, the samples were removed and their infrared spectra were determined. The spectra taken at various time intervals are reported in Figures 23 and 24.

2. Weight loss after isothermal aging of polymer samples at 340°C (644°F), 300°C (572°F), and 260°C (500°F): Duplicate elastomer samples of various cured and filled (40%) elastomers were suspended in a circulating air oven at the specified temperatures and weighed from time to time. Tests were terminated when the samples became brittle. Little discoloration was observed. The results are reported in Table XXXI and represented graphically in Figure 25.

3. Properties of polymers at low temperatures: Compounded and cured elastomers were examined for their low temperature properties. Glass transition temperatures were determined by differential thermal analysis. Brittle points were determined by immersing a polymer sample in an methanol bath, lowering the temperature of the bath by 10°C increments, and bending the sample at each temperature plateau. The temperature at which the sample broke is reported as the brittle temperature. The results are shown in Table XXXII.

TABLE XXXI

WEIGHT LOSS ON ISOTHERMAL AGING OF POLYMERS AT 340°C (644°F), 300°C (572°F), AND 260°C (500°F)

All polymers, unless otherwise indicated, were prepared from oxydi-p-phenylenebis(dimethylsilanol), decamethyl-1,5-dioxa-3,7-diaza-2,4,6,8-tetrasilacyclooctane, compounded with 40 parts Hi Sil 233 and 1.7 parts t-butylperoxy benzoate, and press-cured. All values are the average of two determinations.

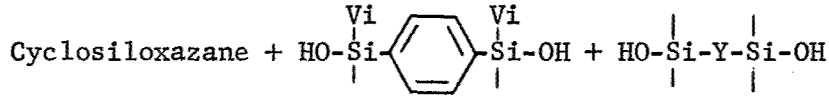
					Weight Loss at 340°C	Weight Loss at 300°C				Weight Loss at 260°C			
Sample	Mole % Vinyl	Parts Hi Sil 233	Parts Mapico Red	Parts Catalyst	67 Hr (%)	70 Hr (%)	144 Hr (%)	171 Hr (%)	243 Hr (%)	96 Hr (%)	192 Hr (%)	480 Hr (%)	672 Hr (%)
1	4.5	40	0	1.7	28.8	15.8		24.0	27.0				
2	2.0	40	0	1.7	26.7	12.6		22.1	26.3				
3[a]	4.5	40	0	1.7	24.6	16.9		25.3	28.1				
4[b]	4.5	40	0	1.2	22.8	13.1		21.9	26.6				
5[c]	2.0	40	3	1.7		14.7	24.8						
6	2.0	40	3	1.7		14.5	24.9						
7	2.0	50	3	1.7		13.7	24.0						
8	2.0	70	3	1.7		13.2	22.3						
9	2.0	40	3	1.7						3.0	5.2	11.6	15.9
10	2.0	40	0	1.7						3.1	5.1	12.0	16.7
11[d]	2.0	40	0	1.7						3.0	4.5	9.4	12.0
12	4.0	40	3	1.7						2.6	5.0	12.5	16.9
13	4.0	40	3	1.2						1.9	-	-	-
14	4.0	40	0	1.7						2.5	4.3	11.8	16.3

a/ Polymer from heptamethyl-1,3-dioxa-5-aza-2,4,6-trisilacyclohexane.
b/ Polymer from nonamethyl-1,3,5-trioxa-7-aza-2,4,6,8-tetrasilacyclooctane.
c/ 280°F cure.
d/ Polymer from p-phenylenebis(dimethylsilanol).

TABLE XXXII

PROPERTIES OF POLYMERS AT LOW TEMPERATURES

Polymer Composition



Cyclosiloxazane	Y	p-Phenylenebis-(methylvinylsilanol) (mole %)	Glass Transition Temperature (°C)	Brittle Temperature (°C)
$(CH_3)_9NO_3Si_4$	$(C_6H_4)_2O$	4.5	-54	-100
$(CH_3)_7NO_2Si_3$	$(C_6H_4)_2O$	4.5	-38	-70
$(CH_3)_{10}N_2O_2Si_4$	$(C_6H_4)_2O$	4.0	-39	-70
$(CH_3)_{10}N_2O_2Si_4$	$(C_6H_4)_2O$	2.0	-39	-80
$(CH_3)_{10}N_2O_4Si_4$	$(C_6H_4)_2O$	None (uncured gum)	-40	-
$(CH_3)_{10}N_2O_4Si_4$	C_6H_4	2.0	-	-100

4. Thermogravimetric analyses: Plots of thermogravimetric analysis traces at different heating rates of a filled and cured polymer based on oxydi-p-phenylenebis(dimethylsilanol), decamethyl-1,5-dioxa-3,7-diaza-2,4,6,8-tetrasilacyclooctane, and 2 mole % p-phenylenebis(dimethylsilanol) are represented in Figure 1. All samples were heated from room temperature at the specified rate except for one sample, which was heated to 350°F at 10°C/min, then to 450°C at 0.625°C/min. The latter procedure introduced some error in that the represented weight losses are probably less at each temperature than the true weight loss would be if the sample had been heated through the entire range at one rate. Such a comparison is provided in Figure 5. Traces for the same polymer at different heating rates in nitrogen are shown in Figure 2.

Weight losses at different heating rates for a filled and cured polymer based on p-phenylenebis(dimethylsilanol), decamethyl-1,5-dioxa-3,7-diaza-2,4,6,8-tetrasilacyclooctane, and 2 mole % of p-phenylenebis(methylvinylsilanol) in air and nitrogen are summarized in Figures 3 and 4, respectively. Activation energies were calculated from the traces in Figures 1-4 according to the method of Flynn and Wall (Ref. 2). Plots at three weight loss levels of $1/T \times 10^{-3}$ against -log β (β = heating rate in °C/sec) were linear at rates of 2.5°C/min, 5°C/min, and 10°C/min. The results of these calculations are summarized in Table XXXIII.

TABLE XXXIII

ACTIVATION ENERGY FOR DECOMPOSITION FOR VARIOUS POLYMERS

Arylenedisilanol	Atmosphere	Estimated Activation Energy (kcal/mole) C = 90	C = 95	C = 97	Average
Oxydi-p-phenylenebis-(dimethylsilanol)	Air	19.2	21.9	16.8	19.3
	Nitrogen	29.0	29.0	30.7	29.6
p-Phenylenebis(dimethyl-silanol)	Air	16.1	15.3	12.5	14.6
	Nitrogen	116.1	114.4	100.9	110.5

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APPENDIX

FIGURES 1 THROUGH 25

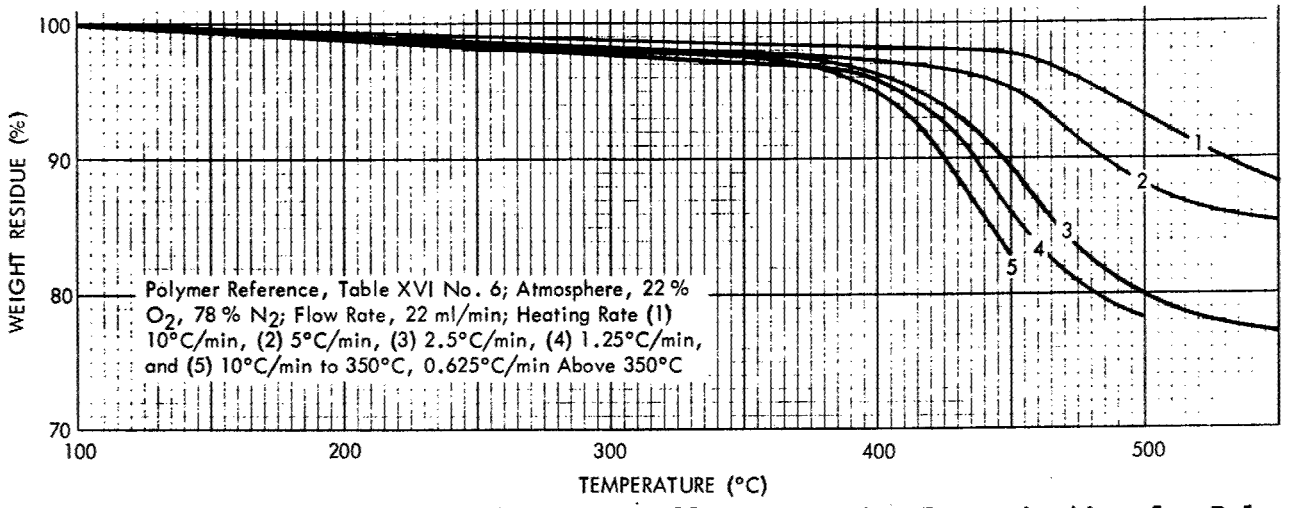


Figure 1 - Thermogravimetric Analyses at Different Heating Rates in Air of a Polymer from Oxydi-p-phenylenebis(dimethylsilanol) and Decamethyl-1,5-dioxa-3,7-diaza-2,4,6,8-tetrasilacyclooctane with 2 Mole % of p-Phenylenebis(methylvinylsilanol)

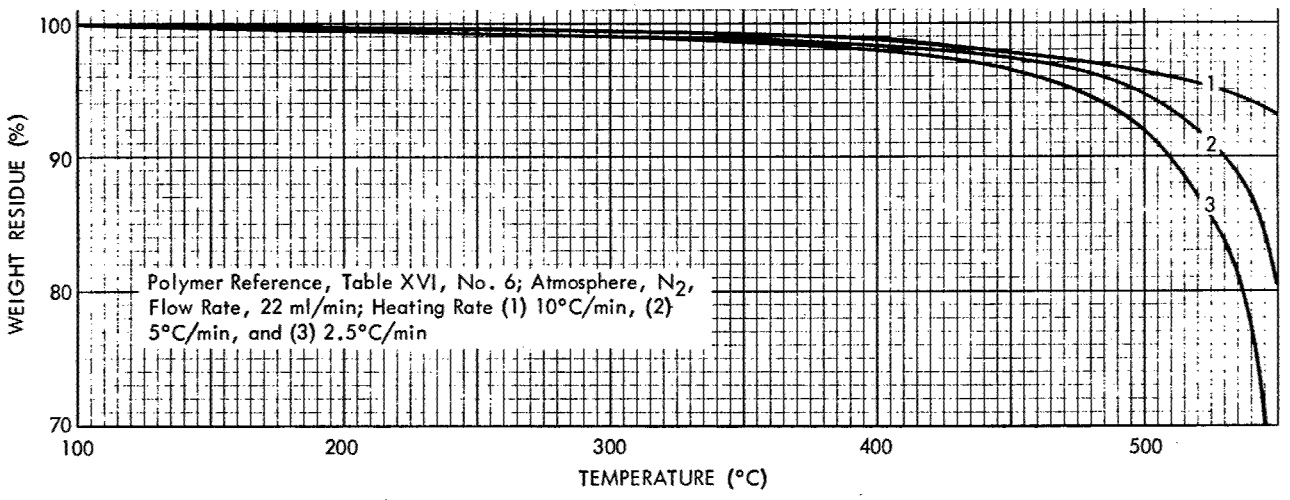


Figure 2 - Thermogravimetric Analyses at Different Heating Rates in Nitrogen of a Polymer from Oxydi-p-phenylenebis(dimethylsilanol) and Decamethyl-1,5-dioxa-3,7-diaza-2,4,6,8-tetrasilacyclooctane with 2 Mole % of p-Phenylenebis(methylvinylsilanol)

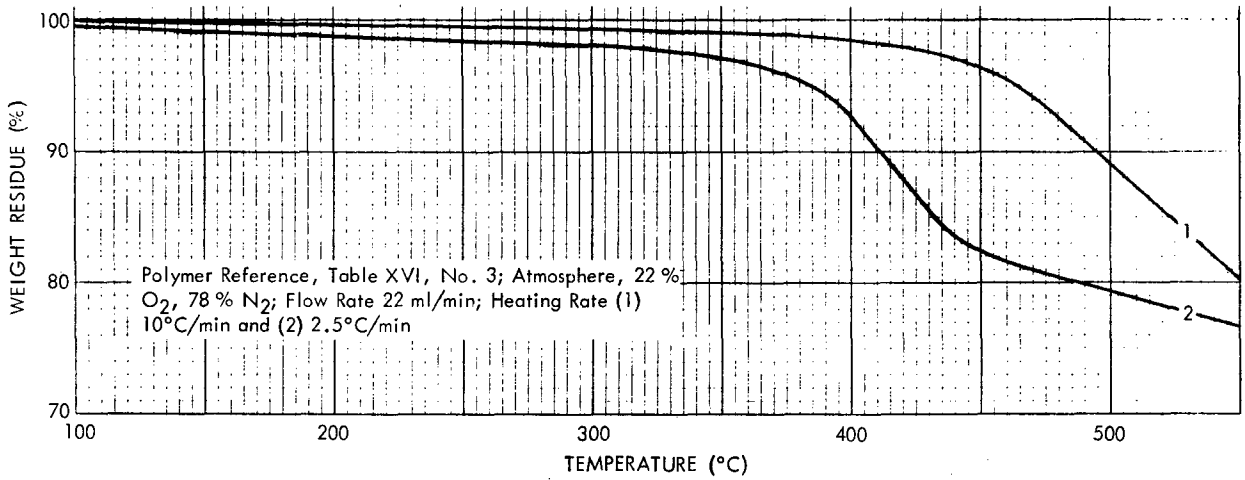


Figure 3 - Thermogravimetric Analyses at Different Heating Rates in Air of a Polymer from p-Phenylenebis(dimethylsilanol) and Decamethyl-1,5-dioxa-3,7-diaza-2,4,6,8-tetrasilacyclooctane with 2 Mole % of p-Phenylenebis(methylvinylsilanol)

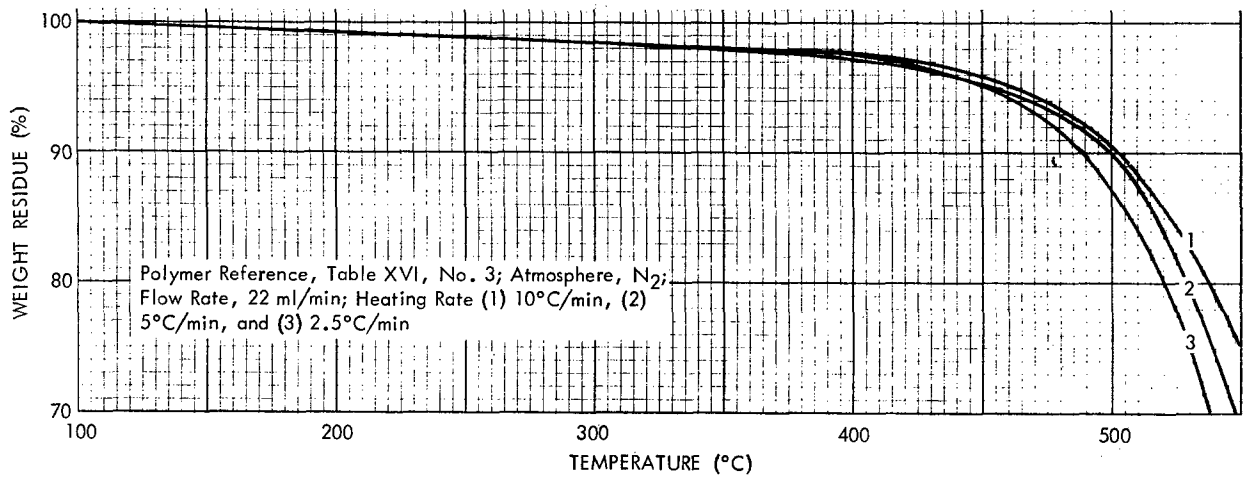


Figure 4 - Thermogravimetric Analyses at Different Heating Rates in Nitrogen of a Polymer from p-Phenylenebis(dimethylsilanol) and Decamethyl-1,5-dioxa-3,7-diaza-2,4,6,8-tetrasilacyclooctane with 2 Mole % of p-Phenylenebis(methylvinylsilanol)

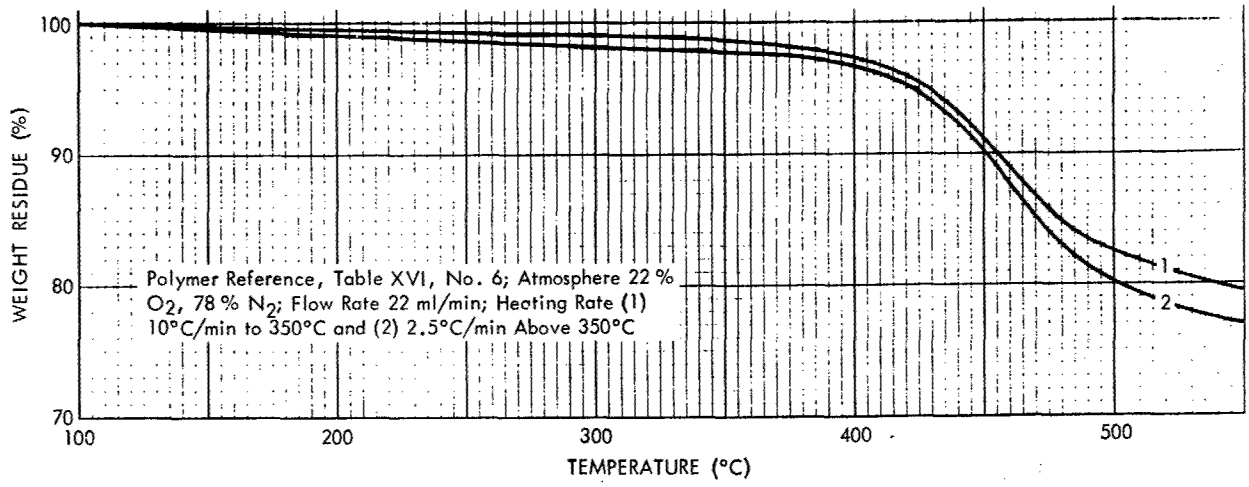


Figure 5 - Thermogravimetric Analyses at Different Heating Rates in Air of a Polymer from Oxydi-p-phenylenebis(dimethylsilanol) and Decamethyl-1,5-dioxa-3,7-diaza-2,4,6,8-tetrasilacyclooctane with 2 Mole % of p-Phenylenebis(methylvinylsilanol)

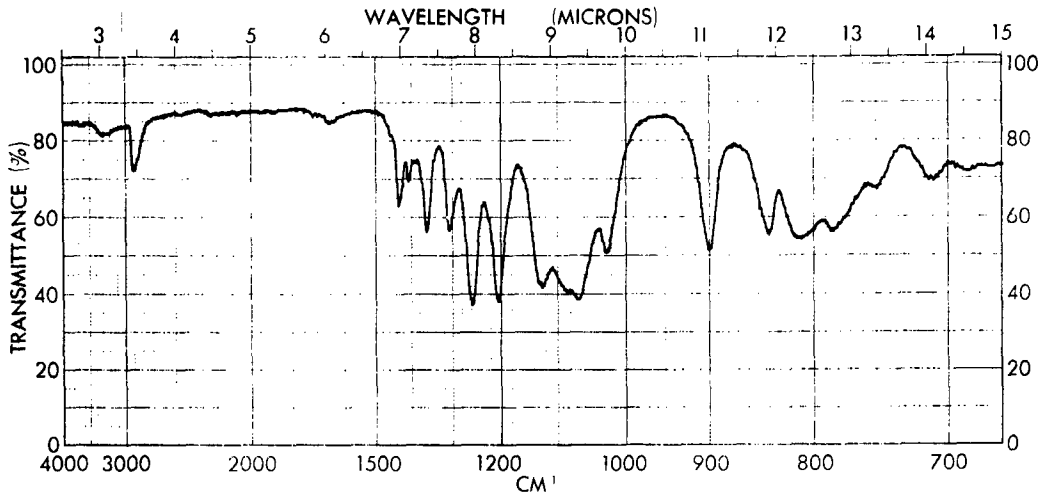


Figure 6 - Infrared Spectrum of 1,3-Bis(3,3,3-trifluoropropyl)-1,3-dichloro-1,3-dimethyldisiloxane (Liquid)

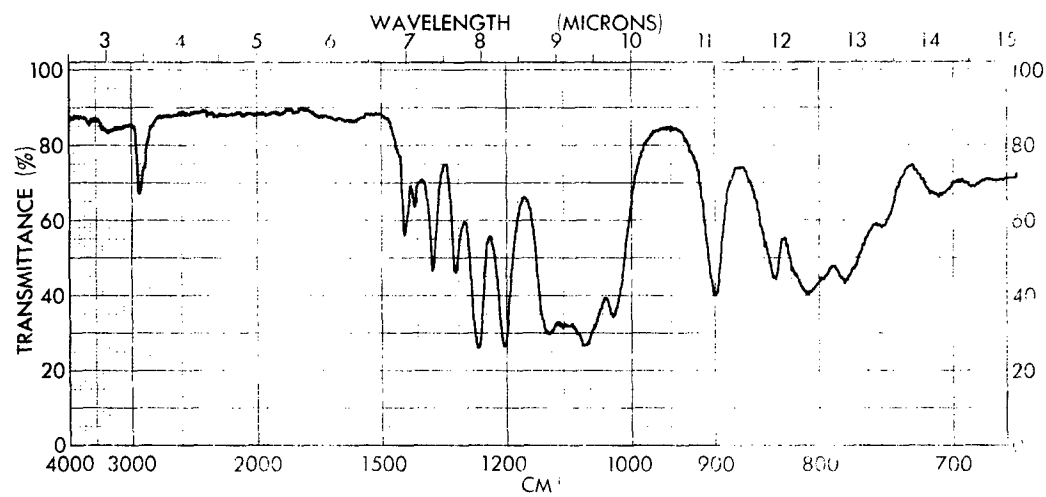


Figure 7 - Infrared Spectrum of 1,5-Dichloro-1,3,5-trimethyl-1,3,5-tris(3,3,3-trifluoropropyl)trisiloxane (Liquid)

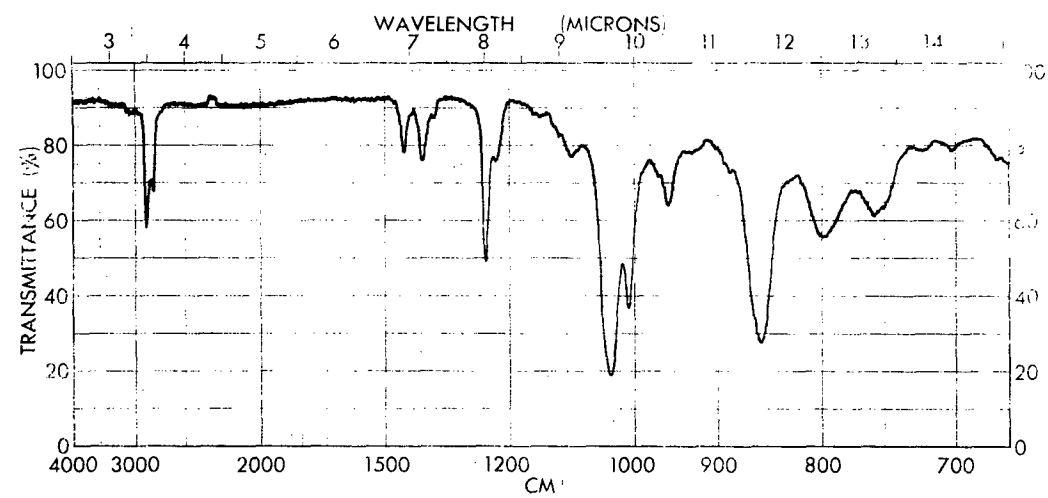


Figure 8 - Infrared Spectrum of N,N'-Bis(chloroethylmethylsilyl)-2,4-diethyl-2,4-dimethylcyclodisilazane (Liquid)

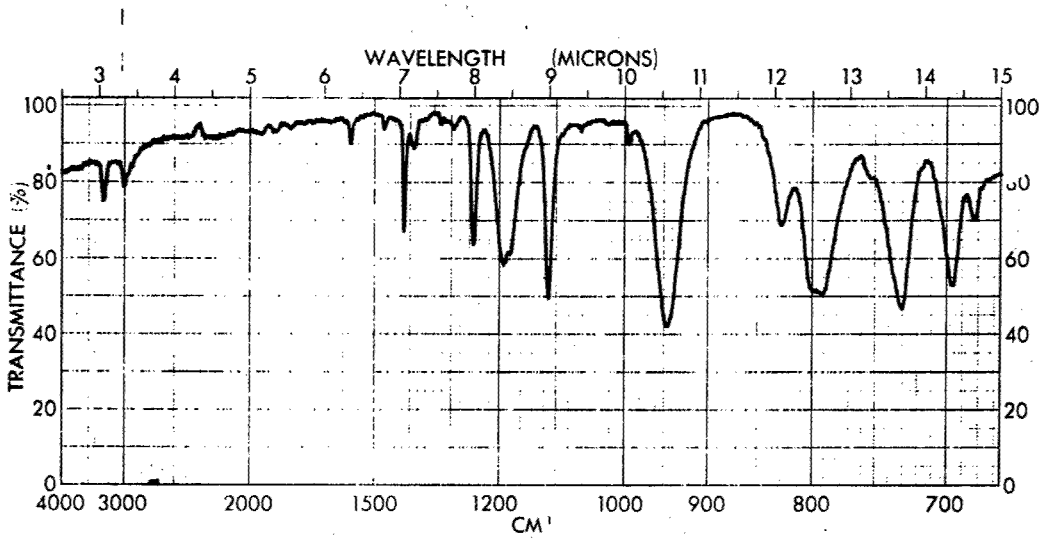


Figure 9 - Infrared Spectrum of 1,3-Dichloro-1,3-dimethyl-1,3-diphenyldisilazane (Liquid)

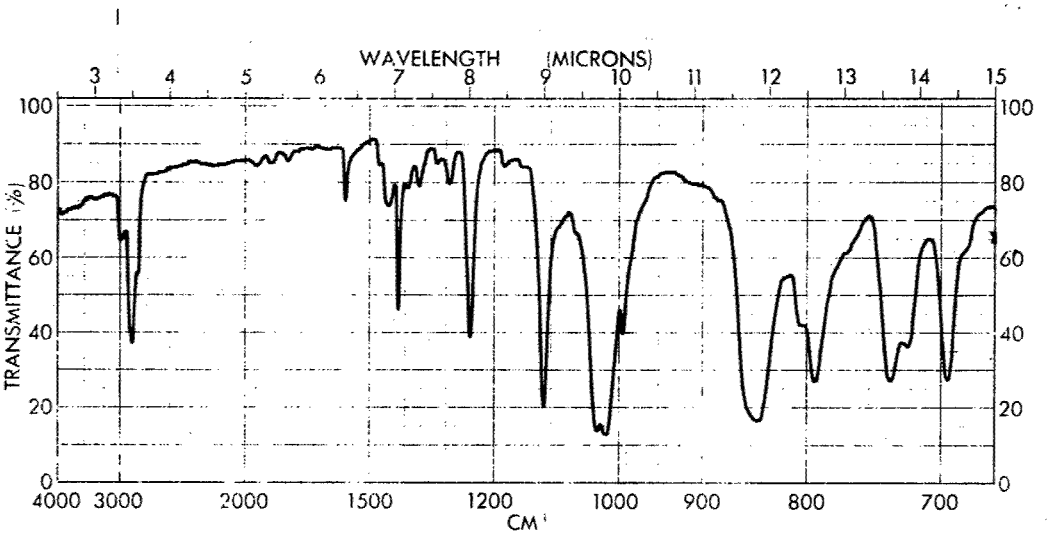


Figure 10 - Infrared Spectrum of N,N'-Bis(chloromethylphenylsilyl)-2,4-dimethyl-2,4-diphenylcyclodisilazane (Nujol)

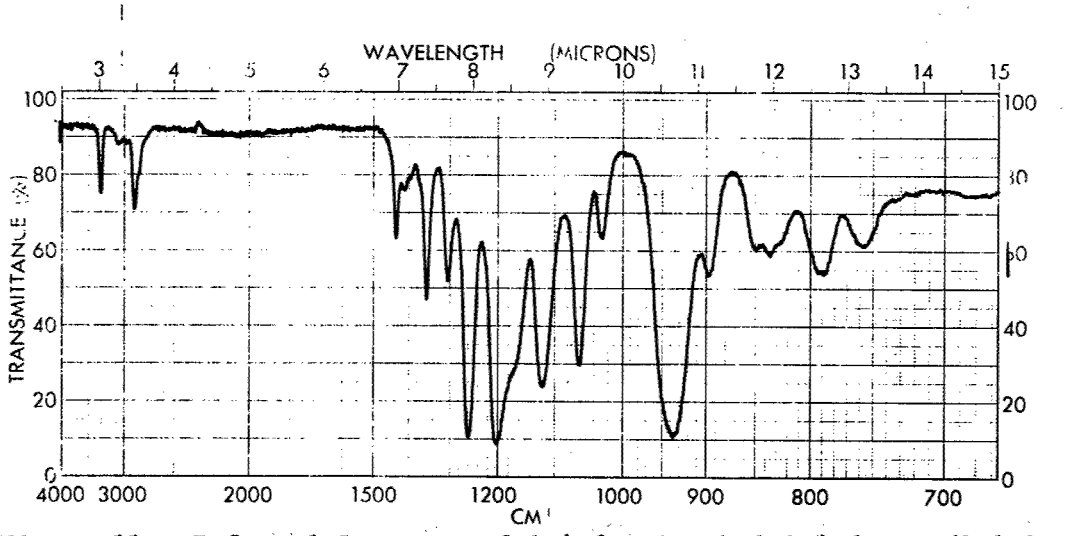


Figure 11 - Infrared Spectrum of 2,4,6-Trimethyl-2,4,6-tris(3,3,3-trifluoropropyl)cyclotrisilazane (Liquid)

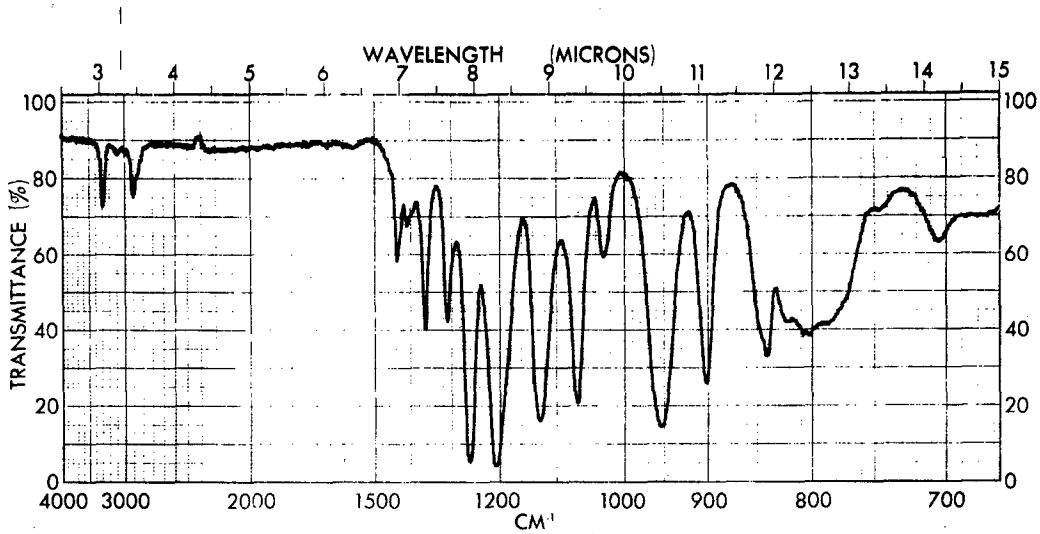


Figure 12 - Infrared Spectrum of 1,3-Bis(3,3,3-trifluoropropyl)-1,3-dichloro-1,3-dimethyldisilazane (Liquid)

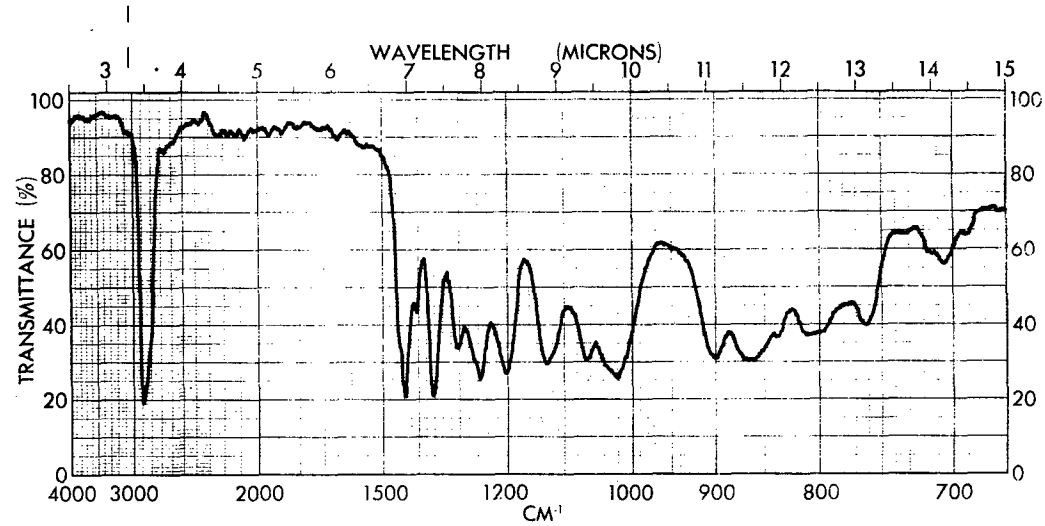


Figure 13 - Infrared Spectrum of N,N'-Bis(chloromethyl-3,3,3-trifluoropropylsilyl)-2,4-bis(3,3,3-trifluoropropyl)-2,4-dimethylcyclodisilazane (Nujol)

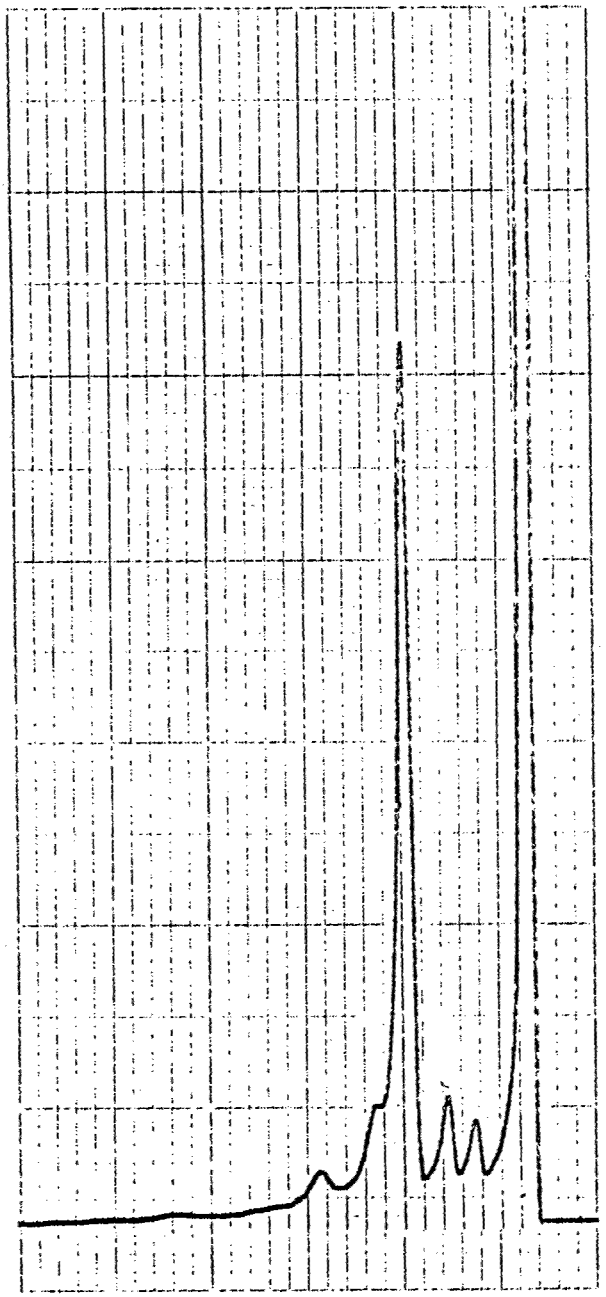


Figure 14 - G.l.c. Analysis of Thrice-Distilled N,N'-Bis(chloromethyl-3,3,3-trifluoropropylsilyl)-2,4-bis(3,3,3-trifluoropropyl)-2,4-dimethylcyclodisilazane

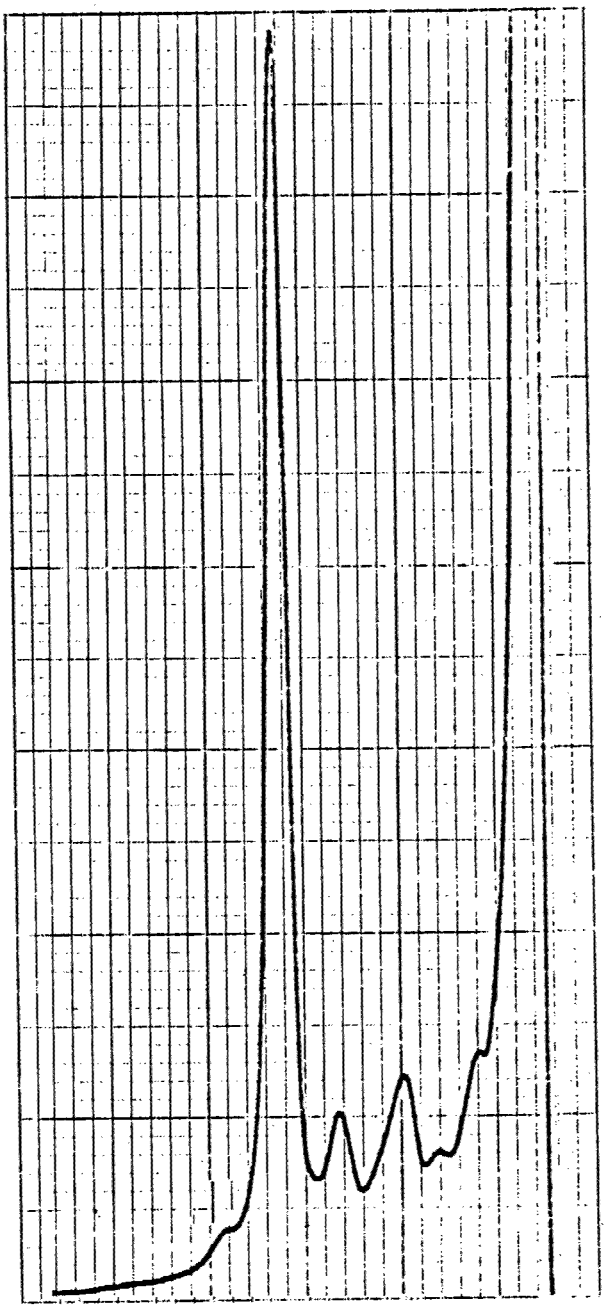


Figure 15 - G.l.c. Analysis of N,N'-Bis-[(dimethylamino)methyl-3,3,3-trifluoropropylsilyl]2,4-bis(3,3,3-trifluoropropyl)-2,4-dimethylcyclodisilazane, m.p. 101-106°C

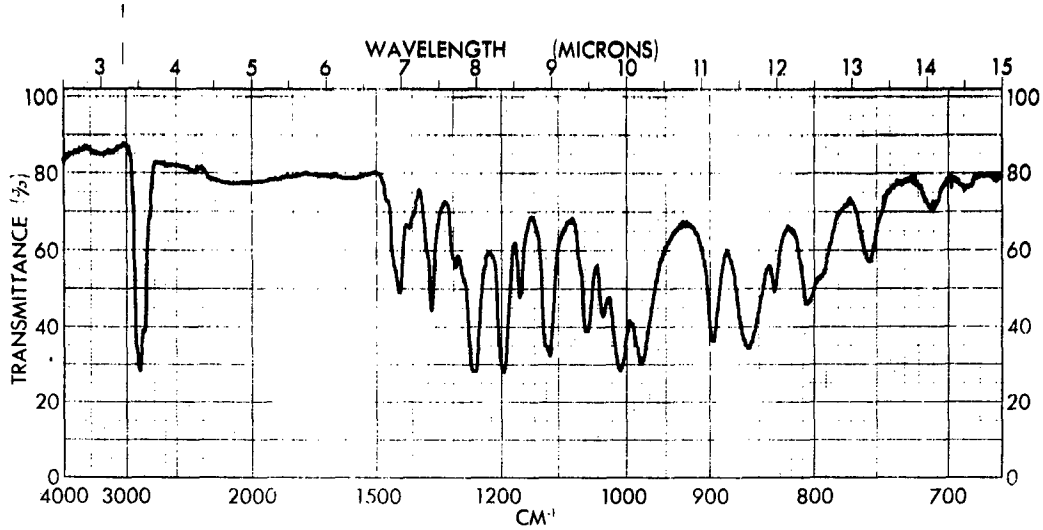


Figure 16 - Infrared Spectrum of N,N'-Bis[(dimethylamino)methyl-3-3,3-trifluoropropylsilyl]2,4-bis(3,3,3-trifluoropropyl)-2,4-dimethyl-cyclodisilazane, m.p. 101-106°C (Nujol)

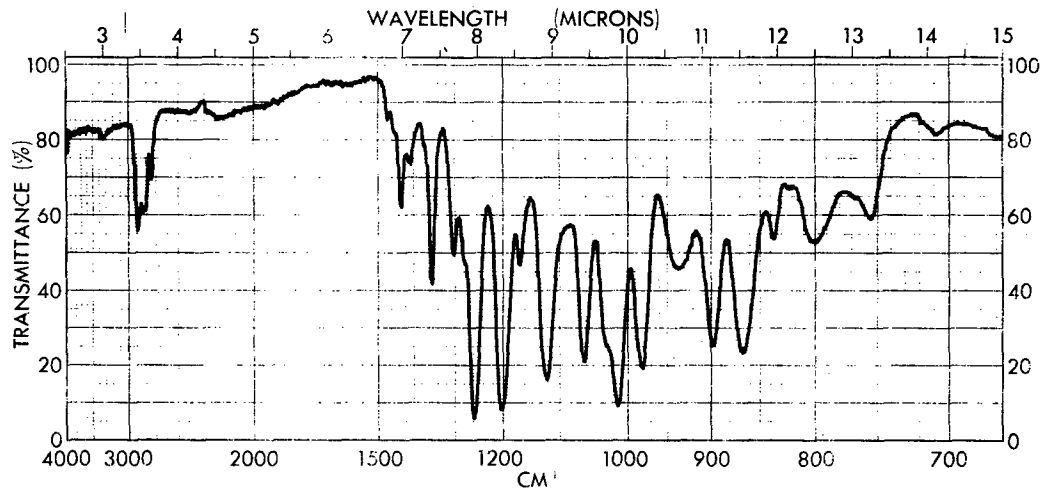


Figure 17 - Infrared Spectrum of N,N'-Bis[(dimethylamino)methyl-3,3,3-trifluoropropylsilyl]2,4-bis(3,3,3-trifluoropropyl)-2,4-dimethyl-cyclodisilazane Not Washed with Petroleum Ether (Liquid)

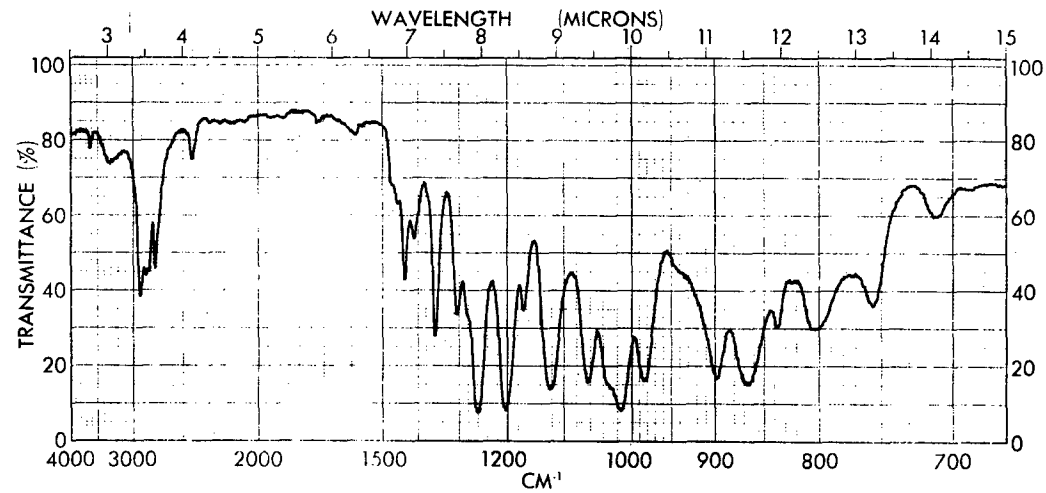


Figure 18 - Infrared Spectrum of N,N'-Bis[(dimethylamino)methyl-3,3,3-trifluoropropylsilyl]2,4-bis(3,3,3-trifluoropropyl)-2,4-dimethyl-cyclodisilazane, Doubly Distilled (Smear)

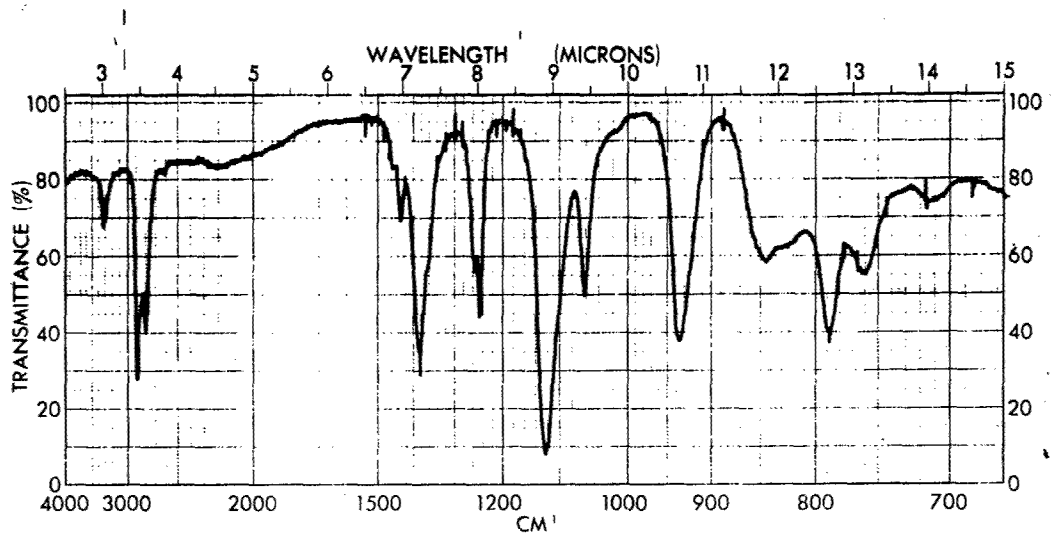


Figure 19 - Infrared Spectrum of Methyltris(ethylamino)silane (Liquid)

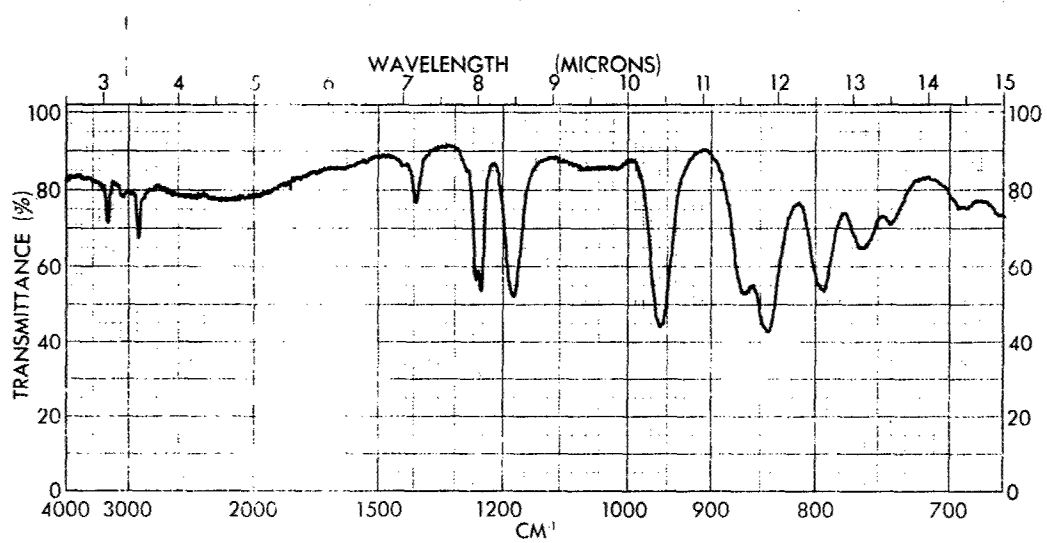


Figure 20 - Infrared Spectrum of a Fraction, Possibly 1,1-Dichloro-1,3,3,3-tetramethyldisilazane (Liquid)

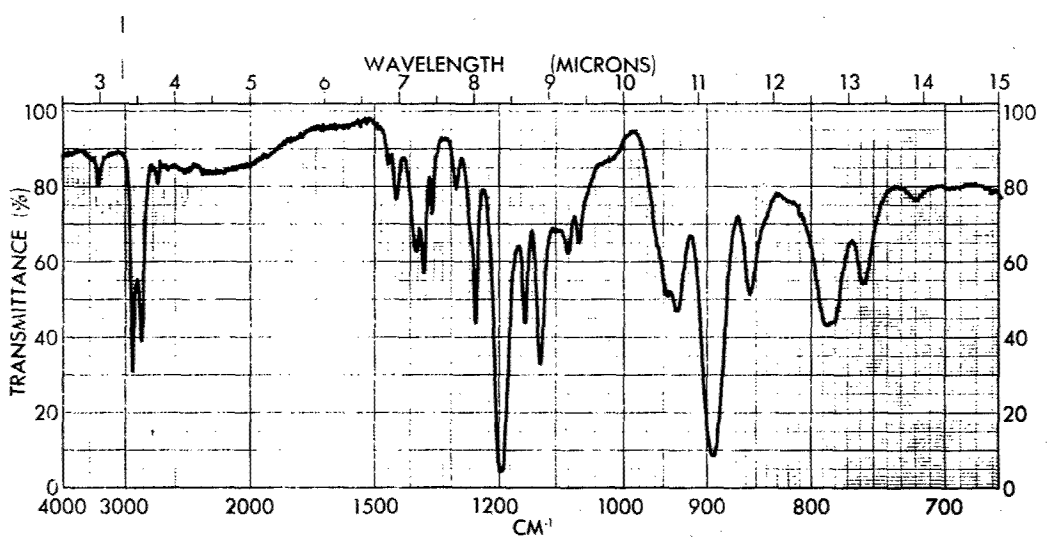


Figure 21 - Infrared Spectrum of 2,5-Bis(ethylamino)-2,5-dimethyl-1,3,4,6-tetraethylspiro[3.3]trisilazane (Liquid)

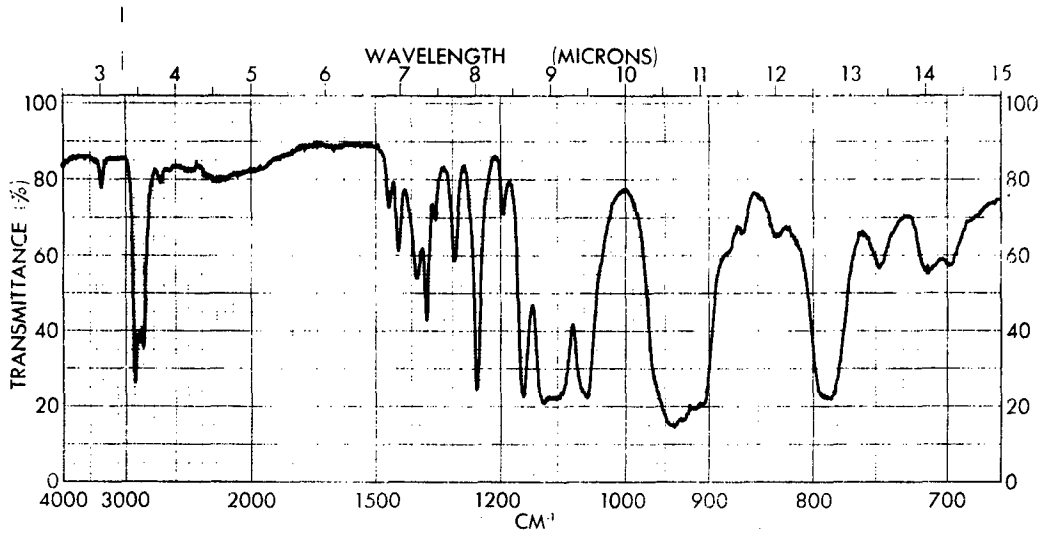


Figure 22 - Infrared Spectrum of the Fraction, b.p. 136-138°C(0.1 mm), From the Thermolysis of Methyltris(ethylamino)silane (Liquid)

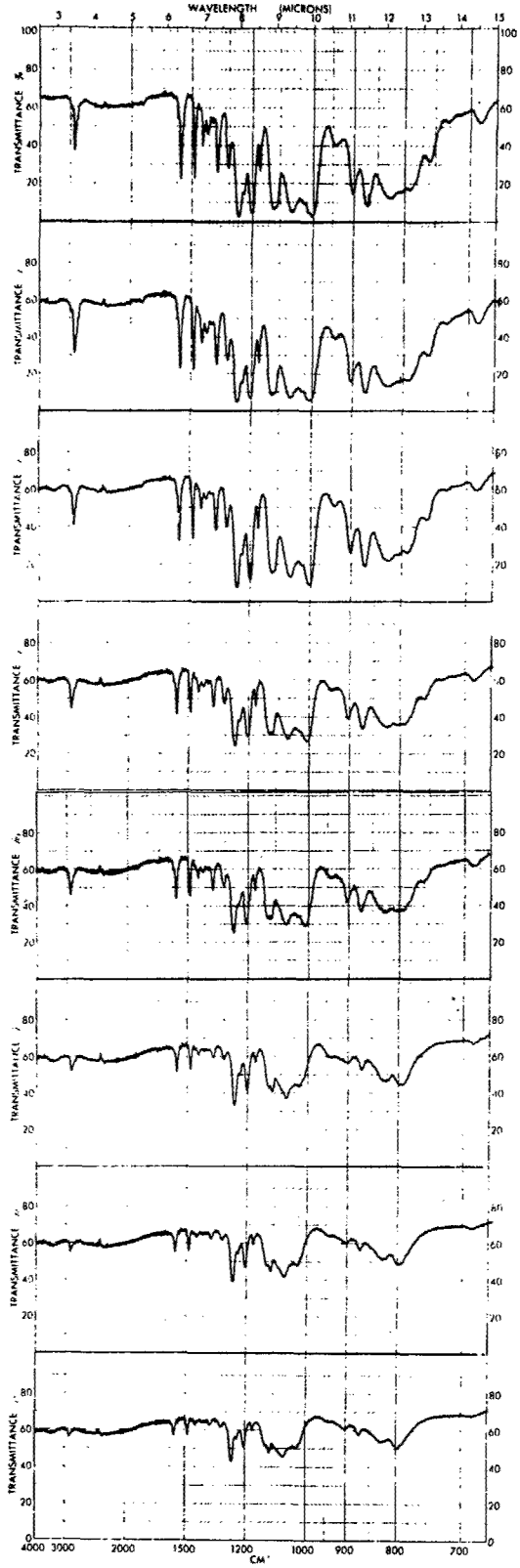
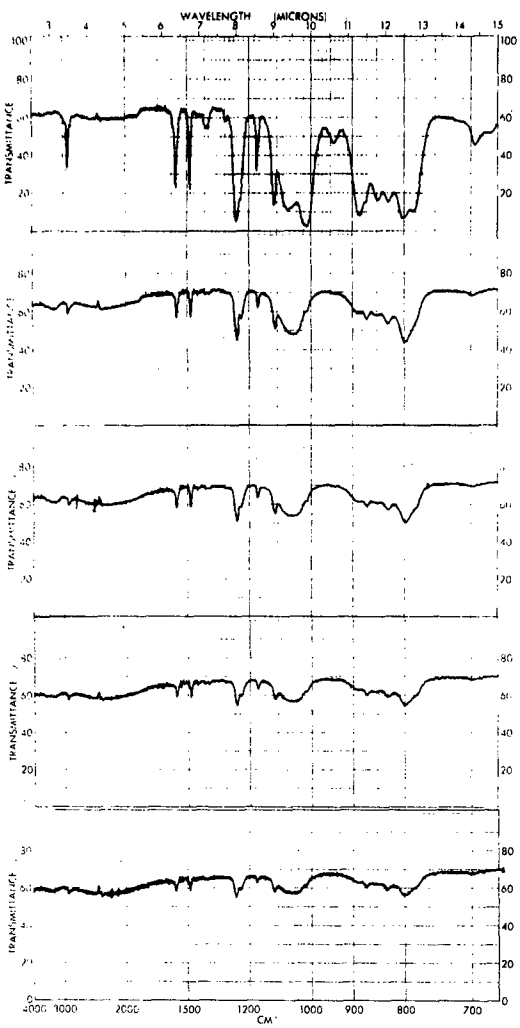


Figure 23 - Infrared Spectra of Polymer Film of an Oxydi-p-phenylene(dimethylsilanol)-N,N'-bis[(dimethylamino)methyl-3,3,3-trifluoropropylsilyl]-2,4-bis(3,3,3-trifluoropropyl)-2,4-dimethylcyclodisilazane Condensate Cast on a KRS-5 Optic After Exposure in a Closed Container with Water at 200°F After Specified Periods of Time



0 Hr

24 Hr

48 Hr

72 Hr

92 Hr

Figure 24 - Infrared Spectra of a Polymer Film of an Oxydi-p-phenylene(dimethylsilanol)-N,N'-bis[(dimethylamino)dimethylsilyl]-tetramethylcyclodisilazane Condensate Cast on a KRS-5 Optic After Exposure in a Closed Container with Water at 200°F After Specified Periods of Time

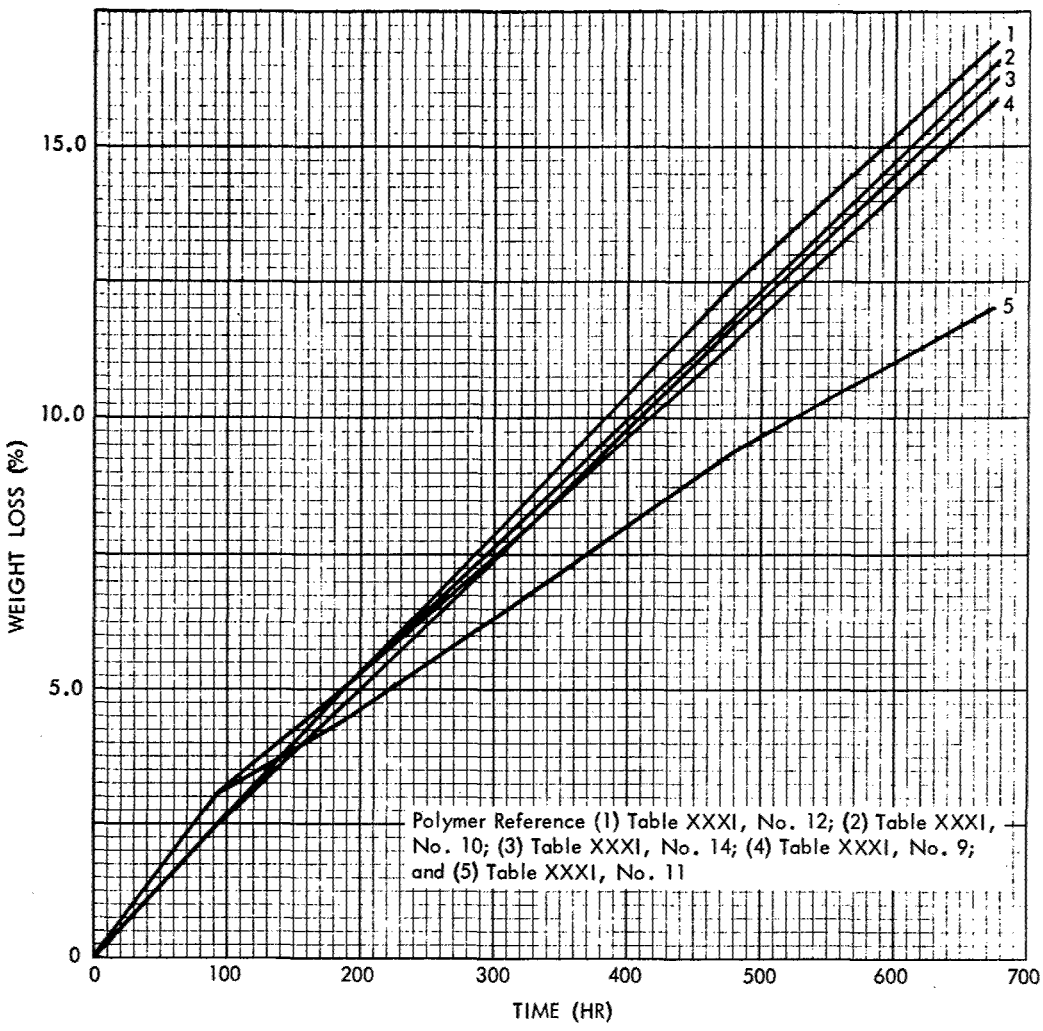


Figure 25 - Isothermal Aging of Experimental Polymers at 260°C

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13. ABSTRACT

If phenothiazine is present in the monomer mixture, arylenedisilanols and cyclosiloxazanes, with p-phenylenebis(methylvinylsilanol) present to insure cross-linking sites, provide polymers with inherent viscosities up to 3.5 dl/g. The polymers can be compounded and cured by conventional procedures. Condensation products of oxydi-p-phenylenebis(dimethylsilanol) and cyclosiloxazanes were studied in detail and elastomers with ultimate tensile strengths of 600-800 psi and 50-150% elongation at break were obtained. Some polymers were also prepared from p-phenylenebis(dimethylsilanol). Depending on the particular structure the polymers retained 15-70% of their strength after 24 hr at 250°C in a closed vessel and 60-80% of their strength after 500 hr in a circulating air oven at 260°C. Exposed to water-saturated air at 65-95°C for 500 hr they retained 45-65% of their strength. Brittle points as low as -100°C were obtained. The first event in the thermal decomposition of these polymers in air is methyl group oxidation. The polymer with the widest range of useful properties was prepared from p-phenylenebis(dimethylsilanol) and decamethyl-1,5-dioxa-3,7-diaza-2,4,6,8-tetrasilacyclooctane. Polymers from arylenedisilanols and cyclodisilazane monomers either gave very low strength elastomers or could not be cured. Improved methods of synthesis for a number of the monomers are reported.

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